A TEXT BOOK OF HEAT

FOR JUNIOR STUDENTS

(INCLUDING KINETIC THEORY OF GASES, THERMODYNAMICS AND RADIATION)

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CHAPTER I

THERMOMETRY

1. Temperature.—The sensation of heat or cold is a matter of daily experience. By the mere sense of touch we can say whether a substance is hotter or colder than ourselves. The hot body is said to possess a higher temperature than the cold one.

But the sense of touch is merely qualitative, while scientific precision requires that every physical quantity should be measurable in numerical terms. Further, the measurements must be accurate and easily reproducible. This requires that the problem should be handled objectively and the sense of touch should be discarded in favour of something which satisfies the above criteria. Let us see how this can be done.

When two bodies are brought in contact, it is found that, in general, there is a change in their properties such as volume, pressure etc. due to exchange of heat. Finally an equilibrium state is attained after which there is no further change. The two bodies are then said to be in *thermal equilibrium with* each other. In this state of thermal equilibrium the two bodies are said to have the same *temperature* which ensures their being in thermal equilibrium. Also it is found that if a body A is in thermal equilibrium with two bodies B and C, then B and C will be in thermal equilibrium with each other and therefore be at the same temperature. These are the two fundamental laws of thermal equilibrium and it is on account of these laws that we are able to measure the temperature of bodies B and C by bringing them successively in thermal equilibrium with the thermometer A. The temperature of a system is a property which determines whether or not a system is in thermal equilibrium with other systems.

Heat causes many changes in the physical properties of matter some of which are well known, *e.g.*, expansion, change in electrical resistance, production of electromotive force at the junction of two dissimilar metals. All these effects have been utilised for the measurement of temperature. The earliest and commonest thermometers utilise the property of expansion. Mercury-in-glass is universally employed as a thermometer for ordinary purposes, but though it is simple, convenient to use and direct-reading, it is not sufficiently accurate for high-class scientific work.

Mercury Thermometer.*—Everybody is familiar with the ordinary centigrade thermometer. It consists of a glass bulb containing mercury to which a graduated capillary stem is attached. The freezing point of water is marked 0°C and the boiling point 100°C and the interval divided into 100 equal parts. This scale was first introduced by Celsius† and is called the Celsius or centigrade scale

* For details of construction see Preston, *Theory of Heat*, Chapter 2.

† Anders Celsius (1701-1744) was born at Upsala where he studied mathematics and astronomy. In 1730 he became Professor of Astronomy and ten years later he built the observatory at Upsala and became its director. He invented the centigrade scale.

and is now adopted for all scientific work. Other scales in ordinary use today are those introduced by Fahrenheit and Réaumur. But Fahrenheit* was the first to choose mercury as the thermometric substance on account of its many advantages. It does not wet glass, can be easily obtained pure, remains liquid over a fairly wide range, has a low specific heat and high conductivity, it is opaque and its expansion is approximately uniform and regular. But we must not forget its several drawbacks. The specific gravity and surface tension of mercury are large, and the angle of contact with glass when mercury is rising is different from that when it is falling. On account of these defects alcohol is sometimes used in place of mercury, and since it has a larger expansion it is more sensitive but is likely to distil over to colder parts of the tube.

The range of an ordinary mercury thermometer is limited by the fact that mercury freezes at $-38{\cdot}8$°C and boils at 356°C but the upper limit can be raised to about 500°C by filling the top of the tube with nitrogen under pressure. The thermometric glass must be of special quality : it should be stable and should rapidly return to its normal state after exposure to high temperatures. The glasses generally employed are *verre dur* and Jena 16^{III} for better-class thermometers and borosilicate glass 59^{III} for high-temperature work.

Mercury thermometers are generally employed for rough work. If they are at all used for accurate work various corrections must be applied to get the true temperature. The important ones among them are the following:—

(1) Correction due to shift of the zero. This is very important since glass after exposure to high temperatures returns to its normal state only after a very long time.

(2) Correction due to change in the fundamental interval from 100 to $100+\delta$ (say) where δ has any value.

(3) Calibration Correction. This is due to want of uniformity in the bore of the capillary tube.

(4) Correction for lag of the thermometer. This increases with the size of the bulb.

(5) Correction due to changes in the size of the bulb caused by variable internal and external pressure.

(6) Correction for the effects of capillarity.

(7) Exposed stem correction. Part of the stem and hence the contained mercury does not acquire the temperature of the bath.

For details concerning the application of these corrections see Appendix I.

3. Special Types of Liquid Thermometers.—The ordinary mercury thermometer is not suitable for certain purposes ; for this reason special types of thermometers have been devised. They are

* Daniel Gabriel Fahrenheit (1686-1736) was born in Danzig of a rich family and finally settled in Amsterdam. He made improvements in the barometer and the thermometer and devised his thermometric scale.

modifications of the ordinary thermometer designed to serve the particular end in view.

Six's Thermometer:

For *meteorological* purposes thermometers are required to indicate the maximum and minimum temperatures to which they have been exposed during a certain period. Six devised a combined maximum and minimum thermometer which is indicated in Fig. 1. The bulb A and part of the tube is filled with alcohol up to the level B, then with mercury up to C above which again there is alcohol up to D. The glass indexes I, I, have each an iron wire attached (shown separately), and placed above B and C in each tube. When the temperature rises the alcohol in A expands and the expanding mercury, on account of its surface tension, pushes upwards the index above C to its maximum limit. With a fall in temperature this index is undisturbed due to the viscosity of alcohol being small while the index above B is pulled upwards by the contracting alcohol, but is left behind when the temperature rises. The iron wire attached to the glass index prevents it from falling under its own weight and enables its position to be adjusted from outside.

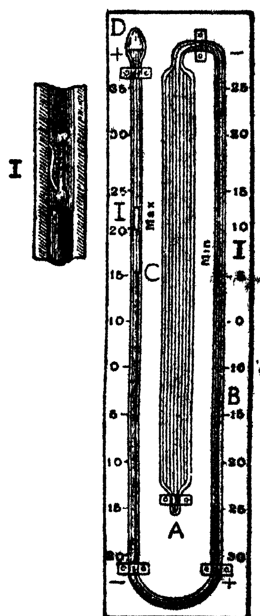


Fig. 1.—Six's maximum and minimum thermometer.

The clinical thermometers in ordinary use are mercury thermometers of short range of the maximum type. The stem just above the bulb has a constriction through which the mercury passes when its temperature rises. On cooling, the mercury is unable to force its way back. The range of temperatures is usually 95°F to 110°F and the bulb is very thin and the capillary bore very fine. The mercury thread is rendered easily visible by constructing lens-front thermometers.

For accurate work, such as the determination of the boiling and melting points of organic substances, several short-range thermometers are employed between the range 0 and 450°C. They are called *chemical* thermometers. Benzol and toluol thermometers are amongst the many that are in use.

The *Beckmann* thermometer, indicated in Fig. 2, is used to measure small changes of temperature with a high degree of accuracy. The stem is here marked from 0 to 5 representing approximately centigrade degrees and every degree is divided into 100 equal parts. There is a reservoir at the top of the instrument, shown separately at (*b*), to enable the range to be varied. To set the thermometer to any desired range the bulb is heated to expel mercury into the reser-

voir and the instrument gently tapped when the mercury column breaks near the reservoir and some mercury is transferred into it. Next the Beckmann thermometer is immersed along with an auxiliary thermometer in a bath whose temperature is varied till the mercury stands at 0 division of the former. The temperature corresponding to the zero of the Beckmann thermometer is thus observed on the auxiliary thermometer, and by varying the amount of mercury in the bulb this is adjusted to be near the desired range. The value of each scale division varies with the quantity of mercury in the bulb and a correction curve for different settings of the zero is supplied with the instrument from which the correction at any point of the scale may be obtained.

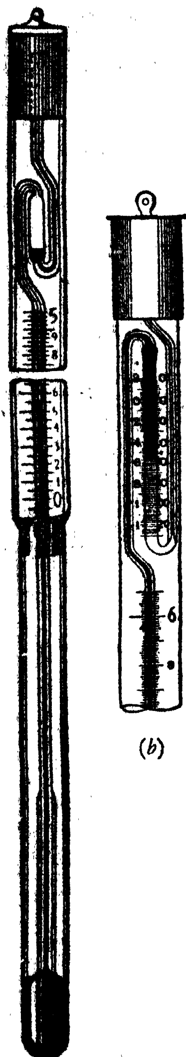


Fig. 2.—Beckmann thermometer.

4. Gas Thermometers.—The fundamental disadvantage of liquid thermometers is that two thermometers containing different liquids such as mercury and alcohol, and graduated as on page 1, will agree probably only at 0°C and 100°C and at no other temperature. This is due to the fact that the expansion of the two liquids is not regular and similar. Thus the mercury thermometer of page 1 would give an arbitrary* scale of temperature. Moreover, the corrections to be applied to it (p. 2) are uncertain and known only approximately. Hence, for accurate work mercury thermometers are calibrated (see Sec. 8) by actual comparison with a resistance thermometer throughout the entire range. Even then the mercury thermometer is rarely used for accurate work, and for all standard work gas thermometers are employed.

Gases possess several advantages as a thermometric substance. (1) Their expansion is large so that gas thermometers will be more sensitive and the expansion of the containing vessel will necessitate only a very small correction. (2) Their expansion is also regular, i.e., the expansion of a volume of gas at 0°C is the same

* The volume v_t of a certain mass of mercury at any temperature t lying between 0 and 100°C as measured on the perfect gas scale is given by the relation

$$v_t = v_0(1 + 1{\cdot}8182 \times 10^{-4}\, t + 0{\cdot}78 \times 10^{-8}\, t^2).$$

Thus the relation is not linear and the readings of the mercury thermometer as calibrated on p. 1 will not agree, even after applying the corrections mentioned on p. 2, with those of a perfect gas thermometer even in the range 0°—100°C.

for every one degree rise of temperature. (3) They can be obtained pure and remain gaseous over wide ranges of temperature. Further, the scales furnished by different gases are nearly identical since the volume and pressure coefficients of all permanent gases are nearly equal. Hence, gas thermometers are used as primary standards with which all others are compared and calibrated.

The theoretical bases underlying the use of gas as thermometric substance are the laws of Boyle* and Charles which are very approximately obeyed by the so-called permanent gases in nature but will be rigorously obeyed by a perfect gas. Let a gas be initially at pressure p_1, volume v_1 and temperature t_1 °C. If we first change its pressure from p_1 to p_2, keeping the temperature constant, and next change the temperature from t_1 to t_2, keeping the pressure constant, we have from these laws,

$$p_1 v_1 = p_2 v'; \quad \frac{v'}{v_2} = \frac{1 + \alpha t_1}{1 + \alpha t_2},$$

where v' is the intermediate volume and α the coefficient of expansion at constant pressure, which is found experimentally to be approximately equal to 1/273. Combining these two equations we have

$$\frac{p_1 v_1}{p_2 v_2} = \frac{1+\alpha t_1}{1+\alpha t_2}, \quad . \quad . \quad . \quad . \quad (1)$$

which is the gas equation.

If $t_2 = -1/\alpha$, $v_2 = 0$, *i.e.*, at the temperature $1/\alpha = 273$°C (nearly) below the ice point, the volume of the gas would be zero provided the perfect gas equation is obeyed throughout the range. This temperature is, by definition, called the *absolute zero*. It is true the gas would liquefy and solidify long before this stage is reached and the perfect gas equation would cease to be valid. Further, it is inconceivable that matter should at any time occupy no space ($v = 0$). Nevertheless the idea of such a zero of temperature is very useful.† If we measure temperatures from this zero, the ice-point is given by $1/\alpha$, the steam point by $(1/\alpha) + 100$, and generally any temperature, t_2°C by $(1/\alpha) + t_2 = T_2$°K. The scale so obtained is called the *Kelvin* or *Absolute Scale* and will be denoted by °K. Hence equation (1) becomes

$$\frac{p_2 v_2}{p_1 v_1} = \frac{(1/\alpha) + t_2}{(1/\alpha) + t_1} = \frac{T_2}{T_1},$$

or

$$\frac{p_2 v_2}{T_2} = \frac{p_1 v_1}{T_1} = \frac{p_0 v_0}{T_0} \text{ (say)}, \quad . \quad (2)$$

where the suffix 0 denotes the quantities at 0°C. The quantity

* Robert Boyle (1627-1691) was born in Ireland but settled in England in 1644. He distinguished himself in the study of Physics and Chemistry and was one of the foundation members of the Royal Society. His main contribution is the law of gases which still bears his name.

† The absolute zero thus defined is shown from thermodynamic considerations (Chap. X) to be the lowest temperature possible. Hence the idea of this absolute zero is very important [see further § 7].

p_0v_0/T_0 is known as the gas constant and varies as the mass of the gas taken, but is approximately the same for equivalent gram-molecules of all gases. For one gram-molecule this quantity is usually denoted by R and is equal to $8{\cdot}3\times10^7$ ergs/degree approximately. If the mass of the gas is increased n times, the volume at the same temperature and pressure will be increased n times and hence the gas constant will also be increased n times. Hence, the gas equation can be written generally in the form $pv=nRT$ where n denotes the number of gram-molecules of the gas.

Equation (2) furnishes two ways of measuring temperature. The pressure may be kept constant and the volume observed at different temperatures giving us the constant pressure thermometer; or the volume may be kept constant and the change in pressure noted, a principle utilised in the constant volume thermometer.

Exercise.—Calculate the pressure of 20 grams of hydrogen inside a vessel of 1 cubic metre capacity at the temperature of 27°C.

[$pv=nRT$ where $n=20/2$. Ans. 0·25 atm.]

5. Callendar Compensated Air-Thermometer.—Accurate measurements with the constant-pressure gas thermometers are difficult as the gas in the connecting tube and the manometer is at a temperature different from that of the bulb. To avoid this Callendar devised the compensated air thermometer. In this instrument (Fig. 3) the pressure of the air in the thermometer bulb B is kept equal to the pressure of the air in D as indicated by the sulphuric acid gauge G. When B is heated, the pressure of the air in B increases and equality of pressure is restored by allowing mercury to flow out from the mercury reservoir S. The volume of the tube connecting B and S is eliminated by attaching to D an exactly similar tube placed close to it. This will be evident from the following consideration:—

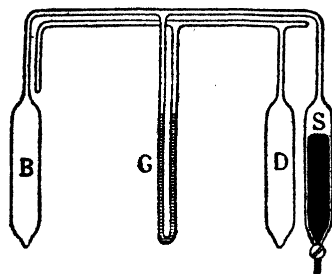


Fig. 3.—Callendar compensated air-thermometer.

Let v, v_1, v_2 be the volume of the bulb B, the tube connecting B and S, and the air in S respectively; θ, θ_1, θ_2, their respective temperatures, n the number of gram-molecules of air contained in B, S and the connecting tube and p its pressure, we have from the gas laws,

$$p\left(\frac{v}{\theta}+\frac{v_1}{\theta_1}+\frac{v_2}{\theta_2}\right)=nR. \qquad (3)$$

Similarly if v', v_1' be the volumes of the air in D and the tube attached, θ', θ_1' their respective temperatures, n' the number of gram-molecules and p' the pressure, we have

$$p'\left(\frac{v'}{\theta'}+\frac{v_1'}{\theta_1'}\right)=n'R. \qquad (4)$$

If $p = p'$, $n = n'$, $v_1 = v_1'$, $\theta_1 = \theta_1'$, we have from (3) and (4)

$$\frac{v}{\theta} + \frac{v_2}{\theta_2} = \frac{v'}{\theta'}.$$

If in addition S and D are immersed in melting ice, $\theta_2 = \theta' = \theta_0$, the freezing point of water, and

$$\theta = \theta_0 \frac{v}{v' - v_2},$$

or denoting v, v', v_2 by B, D, S

$$\theta = \theta_0 \frac{B}{D - S}. \qquad (5)$$

Thus we see that the influence of the connecting tubes is entirely eliminated if (1) the pressure in B is kept equal to that in D ($p = p'$); (2) the total mass of the gas in B, S, and the connecting tube is equal to that in D and the connecting tube ($n = n'$); (3) the volumes of the connecting tubes are equal ($v_1 = v_1'$). The condition ($\theta_1 = \theta_1'$) is automatically satisfied since the two connecting tubes are placed side by side and are at the same temperature.

6. Standard Gas Thermometers.— The constant-pressure air-thermometer has been defended by Callendar on various grounds: (1) the apparatus and the calculations are simple; (2) the internal pressure on the bulb does not increase as the temperature rises; (3) accuracy of the results depends upon the accuracy of weighing. Nevertheless, the instrument does not give concordant results and has been replaced by the constant-volume thermometer as a standard. The normal thermometer selected by the Bureau International des Poids et Mesures and everywhere adopted today is the constant-volume hydrogen ther-

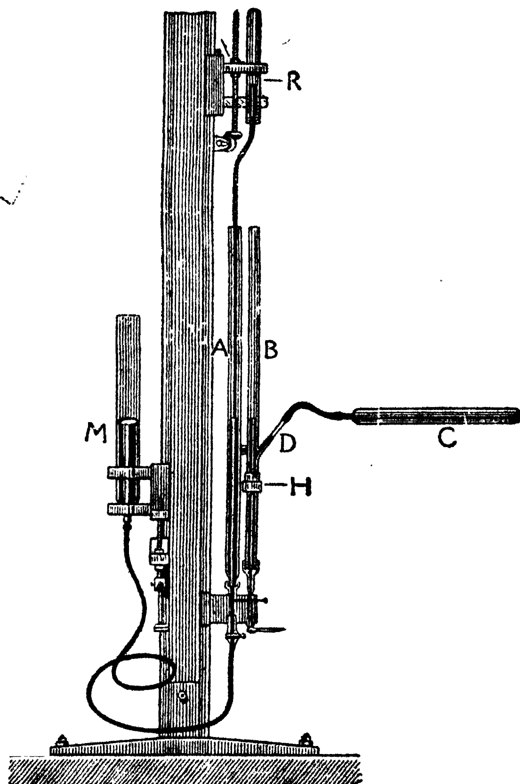


Fig. 4(a).—Constant-volume Hydrogen Thermometer.

mometer filled with gas at a pressure of 1 metre of mercury at the temperature of melting ice. It consists essentially of two parts; the bulb enclosing the invariable gaseous mass and the manometer for measuring the pressure. Fig. 4(*a*) represents the thermometer diagrammatically.

The bulb C is a platinum-iridium tube a litre in capacity, 1 metre in length and 36 mm. in diameter. It is attached to the manometer by a capillary tube of platinum 1 metre in length. The manometer consists of two tubes A and B, and the stem of the barometer R dips into A. The barometer tube is bent so that the upper surface of mercury in it is exactly above B and these levels can be read off by a cathetometer furnished with telescopes. The number of observations to be taken is thus reduced to two. B consists of two columns of mercury separated by the steel-piece H and both these columns communicate with A. By raising or lowering the mercury reservoir M, the mercury surface in the lower part of B is arranged just to touch a fine platinum point P [shown separately in Fig. 4 (*b*)], projecting from the steel-piece H, and thus the volume of the enclosed gas is kept constant.

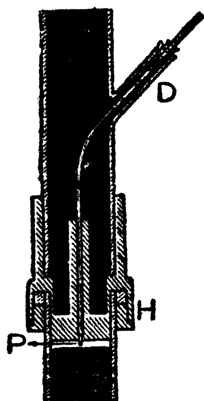


Fig. 4(*b*)

The thermometer described above is suitable for measuring temperatures up to 500°C. For higher temperatures certain modifications are necessary which will be discussed under 'pyrometry' in Chapter XI. The range of gas thermometers with proper modifications can be extended from −260°C to 1600°C.

We shall now deduce a formula for converting the observed pressure readings into corresponding temperatures. If p_0, p_{100} denote the pressure indicated by the manometer at the ice-point and steam-point respectively, then $p_0 v = nRT_0$, $P_{100} v = nR(T_0 + 100)$ where T_0 represents the ice-point on the perfect gas scale and the fundamental interval is 100°C. Hence

$$\frac{p_{100}}{p_0} = \frac{T_0 + 100}{T_0}$$

or

$$\frac{1}{T_0} = \frac{p_{100} - p_0}{100\, p_0} = \beta,$$

where β is the coefficient of expansion at constant volume. Thus we know β for that gas from a measurement of p_{100} and p_0. To find the absolute temperature corresponding to any observed pressure p_1, we have,

$$\frac{p_1}{p_0} = \frac{T_1}{T_0},$$

or

$$T_1 = \frac{p_1}{p_0} \frac{1}{\beta}, \tag{6}$$

since $T_0 = 1/\beta$. Thus to determine an unknown temperature the corresponding pressure p_1 is observed on the thermometer and the temperature T_1 calculated either from the above relation or graphically.

In an actual measurement corrections have to be applied for the following:—

(*a*) The gas in the 'dead space' is not raised to the temperature of the bulb. The 'dead space' consists of the space inside the capillary tube and in the manometer between the mercury level and the steel-piece H. Its initial and final temperatures are also different.

(*b*) Increase in the volume of the bulb C with rise of temperature.

(*c*) Change in volume of the bulb due to changes in internal pressure.

(*d*) Changes in density of mercury on account of temperature changes.

For a discussion of these, the authors' book '*A Treatise on Heat*' may be consulted.

THERMODYNAMIC OR ABSOLUTE SCALE OF TEMPERATURE

7. Perfect Gas Scale.—The formulæ developed for the gas thermometer assume that the gas, in question, accurately obeys the gas laws but experiments show that no real gas does so exactly. The coefficient of expansion α at constant pressure is not exactly the same for real gases as may be seen from any book of physical constants (see Kaye and Laby : '*Physical Constants*'). Further the two coefficients α, β are not exactly equal, and β also varies with the initial pressure. Thus, different gases would furnish different scales of temperature if the thermometer is calibrated as indicated above, and the selection of any particular gas will be arbitrary and will give an arbitrary scale of temperature. To avoid this arbitrariness we must reduce our observations to that state of the gas in which the perfect gas* equation is satisfied.

We shall now indicate the methods† of reducing the observations on real gases to the perfect gas state. This can be done when we have knowledge of the deviation of gases from Boyle's law. The calculations are rather complicated and will not be given here. It is enough to point out that the equation for any real gas can be written in the form

$$pV = RT + Bp + Cp^2 + Dp^3 + \ldots\ldots,$$

where‡ B, C, D...are constants which go on decreasing rapidly. Thus it is evident that at infinitely low pressure ($p \longrightarrow 0$) all gases will obey Boyle's law accurately and this conclusion is borne out by experi-

* A perfect gas is defined as one which will obey Boyle's law and Joule's law (Chap. II, sec. 22) rigorously.

† For fuller information see *A Treatise on Heat* by the Authors.

‡ Further see Chap. IV, Section 1.

mental observation. Now it is experimentally found that the temperature scales, obtained by using the different gases and extrapolating the observations to zero pressure, are actually identical for all the gases. This is the perfect gas scale. The coefficient of expansion α for a perfect gas can be calculated in this manner from the data given by Heuse and Otto. The mean of several results gives $\alpha = 0{\cdot}0036608$ for a perfect gas. Thus T_0 the melting point of ice on the perfect gas scale $= 1/\alpha = 273{\cdot}16°$K. Considering all the available data Birge adopts the value $273{\cdot}16 \pm 0{\cdot}01$. We shall use the value 273 or 273·2 or 273·16 depending upon the degree of accuracy required. Again from some accurate experimental data on oxygen we have

$$\lim_{p \to 0} (pV)_0 = 22{\cdot}414 \text{ litre} \times \text{atmosphere}.$$

Hence
$$R = \lim_{p \to 0} (pV)_0/T_0$$

$$= \frac{22{\cdot}414 \times 10^3 \times 76 \times 13{\cdot}595 \times 981}{273{\cdot}16} \text{ ergs/degree}$$

$$= 8{\cdot}314 \times 10^7 \text{ ergs per degree.}$$

Since 1 calorie $= 4{\cdot}185 \times 10^7$ ergs (Chapter III), hence $R = 1{\cdot}987$ calories per degree. This is the value of the gas constant. For real gases the value of the quantity p_0V_0/T_0 differs only slightly from this.

We may point out here an important result arrived at in Chapter X. There it is shown how Lord Kelvin, from consideration of heat-engines has developed an absolute scale *independent of the property of any particular substance*. This is the standard scale of temperature and is known as the thermodynamic scale. Further it is shown there that this scale is quite identical with the perfect gas scale. We thus see that the perfect gas scale which was hitherto shown to depend on the properties of gases now becomes independent of the properties of any particular substance. Hence it is called absolute scale and is the standard scale adopted in scientific work.

Another method of obtaining the correction to be applied to the real gas scale consists in performing the Joule-Thomson experiment (Chap. VI). But unfortunately the existing data on Joule-Thomson effect are not sufficient to enable us to apply this method and the method given above is almost universally employed.

8. Standardization of Secondary Thermometers.— Gas thermometers are very cumbersome to use and require several corrections. Hence in laboratories they are replaced by secondary standards, such as the resistance thermometer, the thermocouple, etc., which have been carefully standardized by comparison with a standard gas thermometer in standardizing laboratories like the National Physical Laboratory in England or the Bureau of Standards in Washington. For this

purpose, comparison baths may be constructed, each suitable for a particular range. Between 0° and 100°C a water bath, between 80° and 250°C an oil bath, between 250° and 600°C a mixture of potassium nitrate and sodium nitrate, and above that an electrical heater is generally employed.

The secondary thermometers may also be standardized by means of a series of easily reproducible fixed points whose temperatures have been accurately determined. A table of standard temperatures is given below (Table 1.). The values are generally those adopted by the Seventh General Conference of Weights and Measures representing thirty-one nations which was held in October 1927, but some amendments made by the Ninth General Conference in 1948 have also been incorporated.*

9. Fixed Temperature Baths.—It is frequently convenient to calibrate the secondary thermometers by means of the fixed-point scale given in Table 1. The ice-point may be most conveniently obtained by dipping the thermometer in pure melting ice contained in a dewar flask. This is a double-walled glass or metal vessel whose sides are silvered.† For the steam-point the hypsometer indicated in Fig. 5, p. 12 is employed. The diagram explains itself. C is the

Table 1.—*Standard Temperatures.*

Temperature Centigrade	Substance	Temperature Centigrade	Substance
−252·780°	B. P. of Hydrogen	419·5	F. P. of Zinc
−195·81	B. P. of Nitrogen	444·60	B. P. of Sulphur
−182·97	B. P. of Oxygen	630·5	F. P. of Antimony
− 78·5	Sublimation of CO_2	960·8	M. P. of Silver
− 38·87	F. P. of Mercury	1063	M. P. of Gold
0·00	M. P. of Ice	1083	F. P. of Copper
+ 32·38	Transition temperature of Na_2SO_4 $10H_2O$	1453	M. P. of Nickel
		1552	F. P. of Palladium
100·000	B. P. of Water	1769	F. P. of Platinum
218·0	B. P. of Naphthalene.	2443	F. P. of Iridium
231·9	F. P. of Tin	2620 ± 10	M. P. of Molybdenum.
305·9	B. P. of Benzophenone.		
320·9	F. P. of Cadmium	3380 ± 50	M. P. of Tungsten
327·3	F. P. of Lead	3500 ± 50	M. P. of Carbon

* See "The International Temperature Scale of 1948", National Physical Laboratory, Teddington (1949).

† For a complete description see Chap. VI.

condenser employed to prevent the water from being lost by evaporation, M is the manometer and T the thermometer. The path of steam is indicated by arrows. The boiling point of water at the pressure p (in mm. of mercury) is found to be given by the relation

$$t = 100{\cdot}000 + 3{\cdot}67 \times 10^{-2}\,(p - 760) - 2{\cdot}3 \times 10^{-5}\,(p - 760)^2.$$

For other fixed points a number of vapour baths in which sulphur, naphthalene, aniline etc. are used, serves the purpose.

For determining the boiling point of sulphur Callendar and Griffiths found that the standard Meyer-tube apparatus was very suitable. It consists of a hard glass cylinder A of diameter 5 cm. and length about 25 cm. to which a spherical bulb B is attached at the bottom (Fig. 6). The whole is surrounded by an asbestos chamber C. The thermometer T is fitted with an asbestos or aluminium cone

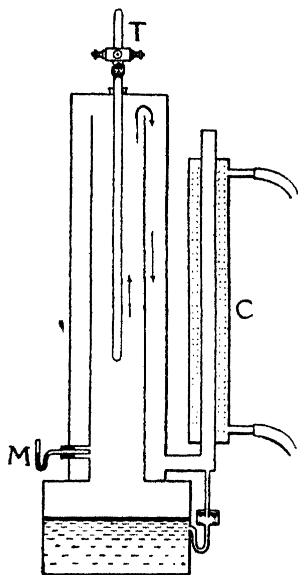


Fig. 5.—Hypsometer.

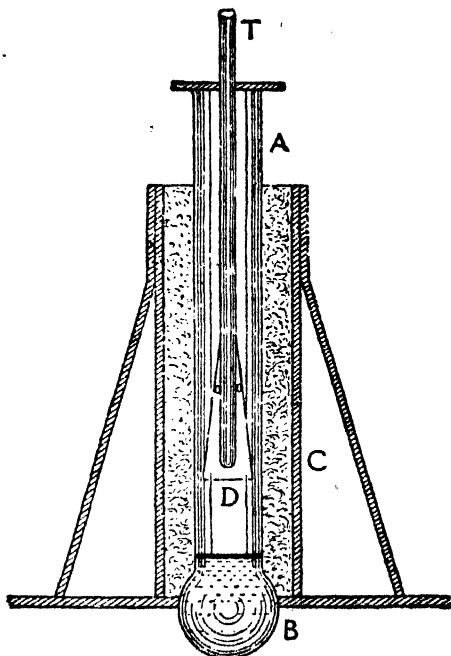


Fig. 6.—Sulphur-boiling apparatus

D. This cone serves in two ways: (1) it prevents the condensed sulphur from running down over the bulb and cooling it below the temperature of sulphur vapour ; (2) it prevents the bulb from directly radiating to the cooler parts of the tube. Sulphur is placed in the bulb and heated over a flame. A side tube may be provided in the upper part of the chamber and serves to condense sulphur vapour. The boiling point of sulphur is given by the formula

$$t = 444{\cdot}60 + 9{\cdot}09 \times 10^{-2}\,(p - 760) - 4{\cdot}8 \times 10^{-5}\,(p - 760)^2.$$

Baths for naphthalene and aniline may be constructed by slightly modifying the above apparatus.

RESISTANCE THERMOMETRY

10. Platinum Thermometers.— The necessity of secondary standards has been clearly indicated above. Two types of such instruments based on two electrical properties of matter will be described in this chapter. These properties are—(1) variation of electrical resistance of metals with temperature ; (2) variation of thermal electro-motive force with temperature. First let us consider the former.

Sir William Siemens was the first to construct thermometer in 1871 based on this principle but the constructional details were unsatisfactory. Later improvements by Callendar* and Griffiths have given the instrument its modern form. Fig. 7 represents an hermetically-sealed thermometer designed by Dr. E. H. Griffiths for laboratory work of high precision. Pure platinum wire free from silicon, carbon, tin and other impurities is selected. It is doubled on itself to avoid induction effects and then wound on a thin plate of insulating mica *m*. The ends of this wire are attached to platinum leads which pass through holes in mica sheets closely fitting the upper part of the tube, and the other ends of these leads are joined to terminals P, P at the top of the instrument. The mica sheets give the best insulation and prevent convection currents of air up and down the tube. The coil is sealed for, otherwise, moisture would deposit on the mica and break down the insulation. To compensate for the resistance of the leads, an exactly similar pair of leads, with their lower ends joined together, is placed close to the platinum thermometer leads, and is connected to terminals marked C, C, on the instrument. These are called compensating leads and are joined in the third arm of the Wheatstone bridge as shown in Fig. 8 (p. 16). Then since the ratio arms are kept equal and the compensating and platinum leads have equal resistance at all temperatures, it is the resistance of the platinum coil alone which is determined. For work up to 700°C copper leads may be used and the whole may be enclosed in a tube of hard glass. But for high temperatures platinum leads must be used and the whole must be enclosed in a tube of glazed procelain.

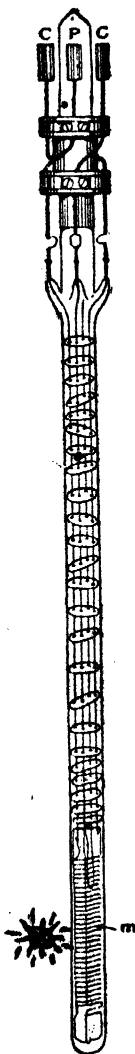


Fig. 7.—Platinum thermometer.

The precision and reliability of modern resistance thermometers are entirely due to the work of Callendar and Griffiths. They deter-

* H. L. Callendar (1863-1930) was educated at Cambridge and worked in the Cavendish Laboratory from 1885 to 1890 on resistance thermometry. His greatest works are the development of the platinum resistance thermometer and the investigation of the properties of steam.

mined the resistance of pure platinum from 0° to 500°C and found that it was very accurately given by a parabolic formula of the type

$$R_t = R_0(1 + \alpha t + \beta t^2), \quad . \quad . \quad . \quad (7)$$

where R_t and R_0 are the resistances at t°C and 0°C and α, β are constants. For pure platinum $\alpha = 3{\cdot}94 \times 10^{-3}$, $\beta = -5{\cdot}8 \times 10^{-7}$. But Callendar further showed that it was unnecessary to solve this quadratic equation to find t from the value of R_t. He gave a special form to this relation and introduced nomenclature which has come into general use. Thus we define the platinum temperature t_p by means of the simple linear relation*

$$R_t = R_0(1 + ct_p),$$

where c is the mean temperature coefficient of resistance between 0° and 100°C. and is thus equal to $(R_{100} - R_0)/100R_0$. The platinum temperature t_p, which is nearly equal to the true temperature t, is, therefore, given by the relation

$$t_p = \frac{R_t - R_0}{R_{100} - R_0} \times 100, \quad (8)$$

where R_t, R_0, R_{100} respectively denote the resistances at t°, 0°, and 100°C. The quantity $R_{100} - R_0$ is called the fundamental interval (F. I.) of the thermometer. Callendar further showed that the difference between the true temperature t and the platinum temperature t_p was accurately given by the parabolic formula

$$t - t_p = \delta \left\{ \left(\frac{t}{100}\right)^2 - \frac{t}{100} \right\}, \quad (9)$$

where δ is a constant for the particular specimen of wire and its value depends upon the purity of the specimen. To deduce (9) we proceed as follows:—

$$t - t_p = t - \frac{R_t - R_0}{R_{100} - R_0} \times 100$$

$$= t - \frac{\alpha t + \beta t^2}{100\alpha + (100)^2\beta} \times 100 \text{ from (7)}$$

$$= -\frac{\beta(100)^2}{\alpha + 100\beta}\left[\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right].$$

Thus δ in equation (9) is equal to

$$-\frac{\beta(100)^2}{\alpha + 100\beta}.$$

The value of δ for the specimens empoyed is about 1·5. The higher the purity the larger is α and the smaller is δ. δ is determined

* c is slightly different from α. The exact relation may be deduced to be

$$\alpha = c\left(1 + \frac{\delta}{100}\right); \quad \beta = -\frac{c\delta}{(100)^2}$$

by finding the platinum temperature t_p for the boiling point of sulphur whose true temperature is known, and then substituting in (9). Knowing δ for a specimen, we can use it to measure any unknown temperature. The resistance R_t of the thermometer at the unknown temperature is found out and then using (8) t_p is determined. From this, using the value of δ, the true temperature t can be determined with the help of (9). It will be observed that the correction term giving the value of $t-t_p$ contains the unknown temperature t. For rough work the value of t_p may be substituted for t on the right-hand side of (9). For accurate work, however, the procedure is as follows:—The right-hand side of (9) is calculated for different assumed values of t and a table is constructed giving the value of this correction term for different values of t_p. With the help of this table the true temperature t corresponding to the experimentally determined platinum temperature t_p is found.

It was shown later by Heycock and Neville, and Waidner and Burgess that if the platinum thermometer is standardized at 0°, 100° and the boiling point of sulpur the parabolic formula (9) gives true readings as far as 630°C.

We shall illustrate the method by a numerical example. Let the resistance of a given platinum thermometer at 0°, 100° and boiling point of sulphur (444·6) be 2·56, 3·56 and 6·78 ohms respectively. It is required to calculate the true temperature when the resistance of the thermometer is 5·56 ohms.

$$t_p = \frac{5{\cdot}56-2{\cdot}56}{3{\cdot}56-2{\cdot}56} \times 100 = 300^\circ\text{C}.$$

t_p for the boiling point of sulphur

$$= \frac{6{\cdot}78-2{\cdot}56}{3{\cdot}56-2{\cdot}56} \times 100 = 422^\circ\text{C}.$$

$$\therefore \quad 444{\cdot}6-422 = \delta \left\{\left(\frac{444{\cdot}6}{100}\right)^2 - \frac{444{\cdot}6}{100}\right\}$$

whence $\delta = 1{\cdot}47$.

From (9) we get for $t = 300$, $t-t_p = 8{\cdot}8$, hence $t_p = 291{\cdot}2^\circ$,

$t = 320$, $t-t_p = 10{\cdot}4$ hence $t_p = 309{\cdot}6^\circ$.

The correction $t-t_p$ for $t_p = 291{\cdot}2^\circ$ is 8·8 and for 309·6 it is 10·4.

Hence for $t_p = 300$ it is $8{\cdot}8 + \dfrac{10{\cdot}4-8{\cdot}8}{309{\cdot}6-291{\cdot}2} \times (300-291{\cdot}2) = 9{\cdot}6$.

Therefore the true temperature t is equal to 309·6°C.

11. Measurement of Resistance.— The determination of temperature by this thermometer involves the accurate measurement of the resistance of the platinum wire. Various special types of resistance bridges are used for this purpose. In order to compensate for the resistance of the leads, a bridge with equal ratio arms is used. Further the bridge should be capable of measuring changes in resistance to a high degree of accuracy for the fundamental interval is generally 1 ohm and measurement of temperature to hundredths of a degree requires resistance measurements to one ten-thousandth of an ohm.

The Callendar and Griffiths bridge* is quite suitable for this purpose. Fig. 8 indicates the connections. Q and S, the ratio arms, are kept equal by the makers of the instrument. R consists of a set of resistances of 1, 2, 4, 8, 16, 32, 64 units. The usual plug contacts are here replaced by mercury cup contacts. L_1 and L_2 are two parallel wires of the same material which can be connected to each other by the contact-maker K. This arrangement is adopted in order to eliminate thermo-electromotive forces. P represents the thermometer and C the compensating leads. The resistance r acts as a shunt and makes the resistance of the wire exactly in the desired ratio. The bridge is adjusted for no deflection of the galvanometer G. Suppose the balance point is obtained with the key K at a distance x from the centre of the wire and the entire length of the wire is $2a$. Then

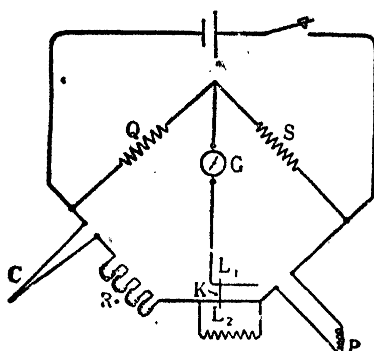


Fig. 8.—Callendar and Griffiths Bridge.

$$P+(a-x)\rho = R+(a+x)\rho$$

or

$$P = R+2x\rho,$$

where ρ is the resistance per unit length of the wire. It is found convenient to select the wire L_2 and the shunt r in such a manner that 1 cm. of the bridge wire has a resistance of 1/200 ohm and the total length of the wire is 20 cm., while the smallest resistance in R marked 1 has a resistance equal to the resistance of the whole wire, i.e., 20/200 = 0·1 ohm. Thus if the fundamental interval of the resistance thermometer is 1 ohm the temperature can be determined correct to ·01°C provided the balance point is determined correct to 0·1 mm. For accurate work, however, various precautions are necessary some of which are given below† :—

(1) The current flowing through the bridge heats the bridge coils and changes their resistance. The change in temperature may be observed on a thermometer and the corresponding change in resistance calculated. The correction can then be easily applied. Or the bridge may be placed in a thermostat.

(2) The thermometer coil has to be very thin (0·15 mm. diameter) since it must have a large resistance and hence the heating effect is considerable. From Callendar's observations the heating effect for a current of ·01 ampere is 0·0016° at 0°C and 0·017° at 100°C. According to him the best procedure is to pass the same current through

* For further details see Flint and Worsnop *'Practical Physics'*.

† For full details *see Methods of Measuring Temperature* by E. Griffiths, (Chap. 3.)

the thermometer at all temperatures when the heating effect remains approximately constant.

(3) The bridge centre must be determined and the bridge wire calibrated.

(4) Due to temperature gradient along the conducting leads and the junctions thermo-electromotive forces are developed in the circuit whose magnitude may be found by closing the galvanometer circuit when the battery circuit is kept open. To eliminate these the galvanometer circuit should be permanently closed and balance obtained for reversals of the battery current. If induction effects are perceptible when the battery circuit is made or broken a thermo-electric key should be employed. This key first breaks the galvanometer circuit, then makes the battery and the galvanometer circuits in succession.

(5) The external leads connecting the terminals PP, CC to the bridge should be exactly similar and similarly placed.

12. As already mentioned the platinum thermometer is standardized by measuring the resistance at the melting point of ice, boiling points of water and sulphur. The last gives δ and hence t can be determined from any subsequent determination of t_p . Eqn. (9) however does not hold much above 630°C and therefore every such thermometer is provided with a calibration curve drawn by an actual comparison with a standard gas thermometer in standardizing laboratories. The temperature can be directly read from this temperature-resistance curve.

The great advantage of platinum thermometers lies in their wide range (−200°C to 1200°C). If carefully prepared, their readings are reliable to 0·01° up to 500°C and to 0·1° up to 1200°C but generally it is not desirable to use them above 1000°C owing to the danger of contamination by the insulating materials. They are free from changes of zero for the wire when pure and well-annealed has always the same resistance at the same temperature. They are very convenient for ordinary use and, when once standardized by comparison with a gas thermometer, they serve as reliable standards. They are often employed to measure small *differences* of temperature very accurately, sometimes even to one ten-thousandth of a degree. There are, however, some drawbacks also. The resistance thermometer has a large thermal capacity and the covering sheath has a low thermal conductivity and therefore the thermometer does not quickly attain the temperature of the bath in which it is immersed. Further some time is lost in balancing the bridge. For these reasons the resistance thermometer is useless for measuring rapidly-changing temperatures. Further impurities in the platinum do not obey the same resistance-temperature law as the pure metal.

Table 2 gives the variation in resistance of a platinum thermometer over a wide range. It is taken from Henning's *Temperaturmessung*. The value of the quantity $R = R_t/R_0$ is given for various

temperatures where R_t, R_0 are the resistances at temperatures t°C and 0°C respectively.

Table 2.—Values of $R = R_t/R_0$.

Temp. °C	R	Temp. °C	R	Temp. °C.	R
−190	0·21607	+40	1·15796	280	2·06661
−180	0·25927	60	1·23624	300	2·13931
−160	0·34505	80	1·31406	320	2·21154
−140	0·42986	100	1·39141	340	2·28330
−120	0·51347	120	1·46830	360	2·35460
−100	0·59612	140	1·54471	380	2·42543
− 80	0·67814	160	1·62067	400	2·49580
− 60	0·75948	180	1·69616	420	2·56570
− 40	0·84019	200	1·77118	440	2·63513
− 20	0·92033	220	1·85474	460	2·70410
0	1·00000	240	1·91983	480	2·77261
20	1·07921	260	1·99345		

THERMO-ELECTRIC THERMOMETRY

13. Thermo-Couples.—Let us now return to the second electrical property utilised for temperature measurement. Starting from Seebeck's discovery in 1821 numerous attempts were made to construct a thermometer based on this principle, for instance, by Becquerel, Pouillet and Regnault. At present thermo-electric thermometry has attained a degree of precision inferior only to resistance thermometry below 1000°C, but for temperatures exceeding that, it is the only sensitive and convenient electrical method at our disposal.

A thermo-electric thermometer installation consists of the following parts :—

(1) The two elements constituting the thermo-couple.

(2) The electrical insulation of these wires and the protecting tubes.

(3) Millivoltmeter or potentiometer for measuring the thermo-electromotive force.

(4) Arrangement for controlling the cold-junction temperature.

The choice of the elements constituting the couple is determined by the temperature to which the couple is to be heated and the e.m.f. developed. For low temperatures up to 300°C couples of base metals such as iron-constantan and copper-constantan are satisfactory, as they develop a large e.m.f. of about 40 to 60 microvolts per degree. For high temperatures these base metals cannot be used as they get oxidized and melt. Nickel-iron couple may be used up to 600° while nickel-nichrome and chromel-alumel thermo-couples can be used up

to 1000° but above that platinum and an alloy of platinum with iridium or rhodium must be used. Le Chatelier in 1886 introduced the couple consisting of pure platinum and an alloy of 90 per cent Pt and 10 per cent Rh which is now largely employed for scientific work. The e.m.f. developed by these noble metals is, however, much less.

The two elements are taken in the form of a wire and one end of both is welded together electrically or in an oxyhydrogen flame. This end *a* (Fig. 9) forms the hot junction. The portions of the wires near the hot junction are insulated with capillaries of fireclay (or hard glass for lower temperatures) and are threaded through mica discs enclosed in outer protecting tube of procelain, quartz or hard glass, depending upon the temperature for which it is meant. The protecting tube prevents the junction from contamination but necessarily introduces a lag. For rough use this may be further enclosed in a steel sheath (shown black in the figure). Where there is no risk of contamination, the mica discs and the protecting tubes can be dispensed with. The wires are connected to terminals C_1 and C_2 on the instrument. To these terminals are connected flexible compensating leads leading to the cold junction (Fig. 10a). These leads are usually of the same material as the elements of the couple itself. Thus the cold junction is transferred to a convenient distant place where a constant temperature, say 0°C, can be maintained. Usually the compensating leads are marked so that there is no difficulty in connecting to the proper terminals.

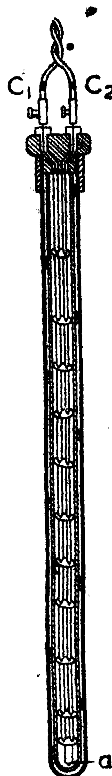


Fig. 9.—Thermo-couple.

There are two ways of making the connections which are indicated in Figs. 10 (*b*) and (*c*). The diagrams explain themselves. The cold junction is immersed in ice at 0°C. As a recording instrument either a millivoltmeter or a potentiometer is employed.

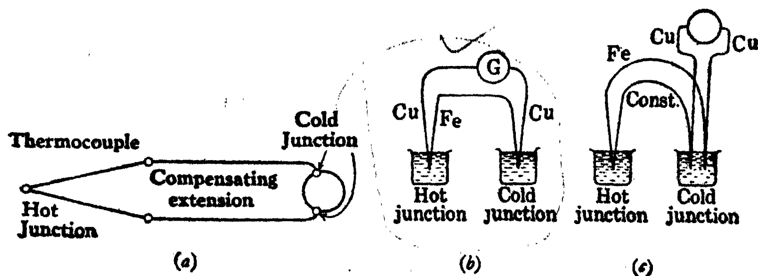


Fig. 10.—Measuring with a thermo-couple.

14. To find the temperature of the hot junction we must measure the e.m.f. developed between the ends of the copper leads.

This can be done by means of a high resistance millivoltmeter which may be graduated to read temperatures directly and the temperature thus obtained can be relied upon to about ± 5°C. For attaining higher accuracy a potentiometer must be used. This arrangement essentially consists of a number of resistance coils A (Fig. 11) placed in series with a long wire resistance r stretched along a scale. A current from the battery E flows through these resistances and its strength is so adjusted by varying R that the potential difference across a fixed resistance K balances against the e.m.f of a standard cadmium cell C (1·018 volts). The e.m.f. developed by the thermo-couple Th is balanced as indicated. The potentiometer can be made direct reading by keeping K = 101·83 ohms. Thus there is a fall of 1 volt per 100 ohms and by constructing the smallest resistance coil of 0·1 ohm resistance and the wire r also of the same resistance, the total e.m.f. across the wire will be 1 m.v. If the wire is divided into 100 divisions and in addition has a sliding vernier having 10 divisions the readings can be taken correct to 1 microvolt.

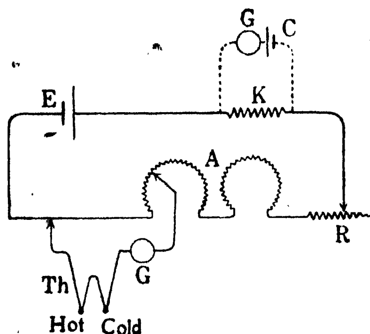


Fig. 11—Illustration of the principle of potentiometer.

Various types of potentiometers based on this principle have been devised specially for this purpose.* With these instruments the e.m.f. can be measured accurately to 1 microvolt which corresponds to about 1°C for a Pt—Pt-Rh couple. For a copper-constantan couple this corresponds to about 1/40 degree. With a sensitive arrangement it is possible to measure to 0·1 microvolt when the sensitiveness is increased about ten times. For accurate work the cold junction must be maintained at 0°C otherwise corrections† will be required in that respect.

In order to deduce the temperature from an experimental determination of the e.m.f. a calibration curve is generally supplied with the instrument. This gives the temperature corresponding to different electromotive forces developed and has been drawn by the makers by an actual comparison with a standard thermo-couple throughout the range. If it is required to calibrate a thermo-couple in the absence of a standard one, the fixed points (Sec. 8) must be utilised. The e.m.f. at those points is measured and an empirical interpolation formula employed in order to give the e.m.f. corresponding to the

* A description of these will be found in *Methods of Measuring Temperature*, by E. Griffiths.

† See Ezer Griffiths, *Methods of Measuring Temperature*, (1947), p. 74.

intermediate temperatures. For a Pt—Pt-Rh couple three different equations must be used for the different ranges. Thus

$$\text{from } 0^\circ \text{ to } 400^\circ\text{C}, \; E = At + B(1 - e^{ct}),$$
$$300^\circ \text{ to } 1200^\circ\text{C}, \; E = -A' + B't + C't^2,$$
$$1100^\circ \text{ to } 1750^\circ\text{C}, \; E = -A'' + B''t + C''t^2,$$

where A, B, C are constants whose values are empirically determined.

Thermo-couples are frequently employed for laboratory work since they are cheap and can be easily constructed. They can be used for the measurement of rapidly-changing temperatures since the thermal capacity of the junction is small and hence the thermometer has practically no lag. Another advantage in the use of thermo-couples is that they measure the temperature at a point—the point at which the two metals make electrical contact. Its chief disadvantage lies in the fact that there is no theoretical formula which can be extrapolated over a wide range and consequently every thermo-couple requires separate calibration.

The useful range of thermo-electric thermometers is about −200° to 1600°C. Readings are reliable only when the composition of the couple does not change even slightly. In actual practice frequent calibration is necessary.

The following are the chief sources of error in thermo-electric thermometry :—

(1) Parasitic electromotive forces developed in the circuit. They are due to (*a*) Peltier-effect or e.m.f. developed due to heating of junction of dissimilar metals at points of the circuit other than the hot and the cold junctions. This occurs often in the measuring apparatus ; (b) Becquerel effect or e.m.f. generated due to inhomogeneities in a single wire ; this occurs mainly in the thermo-couple wires. The e.m.f measured is a sum of these quantities and the Peltier e.m.f. at the two junctions and the Thomson e.m.f. along homogeneous wires of the thermo-couple with ends at the two temperatures. The undesirable effects mentioned in (*a*) and (*b*) must be eliminated by the use of materials and methods free from these effects since they are not taken into account in any thermo-electric formulæ.

(2) Leakage from the light mains or furnace circuit. If leakage currents pass through the potentiometer their presence can be detected by short-circuiting the thermo-couple when the galvanometer continues to be deflected.

(3) Cold-junction correction if it is not kept at 0°C.

For the methods of minimising or eliminating these errors the reader is referred to *Measurement of High Temperatures* by Le Chatelier and Burgess.

Table 3 compiled from various sources gives the thermo-electric e.m.f. for various couples in common use. The cold junction is maintained at 0°C, and the hot junction at t°C. The e.m.f. of the thermo-couple AB being positive means that the current flows from A to B at the cold junction.

Table 3.—E.m.f. in Millivolts for some thermo-couples.

Temp. t°C.	90Pt-10Rh against Pt	Ag/Ni	Ag/Pt	Fe/cons-tantan	Cu/cons-tantan
−200				−8·27	−5·539
−100				−5·82	3·349
− 80		−1·68	−0·30	...	...
0	0·000	0·00	0·00	0·00	0·000
+100	+0·643	+2·18	+0·72	+5·40	+4·276
200	1·436	+4·96	+1·73	10·99	9·285
300	2·315	7·52	2·96	16·56	14·859
400	3·250	9·83	4·47	22·07	20·865
500	4·219	12·04	6·26	27·58	
600	5·222	14·50	8·25	33·27	
700	6·260	17·30	10·60	39·30	
800	7·330	20·73	13·17	45·72	
900	8·434	24·19	15·99	52·29	
1000	9·569			58·22	
1200	11·924				
1400	14·312				
1600	16·674				
1700	17·841				

15. Certain methods of measuring temperature utilise the radiation emitted by the hot body whose temperature is to be measured. These methods will be discussed in detail later (see Chap. XI). They can be used for measuring temperatures from about 1000°C to any upper limit.

16. Certain other methods of measuring temperature utilise any one of the following properties of matter :—

(1) Expansion of a bar of metal.
(2) Changes in vapour density with rise of temperature.
(3) Variation of refractive index of a gas with temperature in accordance with Gladstone and Dale's law.
(4) Calorimetric methods based on the measurement of quantity of heat.
(5) Change of vapour pressure with temperature.

17. Low Temperature Thermometry.*— The standard thermometer in this range is the constant volume hydrogen or helium thermometer. The difficulty in this case is that gases liquefy and even solidify at these low temperatures. Prof. Dewar, however, showed that the boiling point of hydrogen as indicated by the hydrogen thermometer was −253·0°C and −253·4°C, while a helium thermometer registered −253·7°C and −252·1°C. Similarly he compared

* For pyrometry see Chap. XI.

thermometers of other gases. These experiments evidently led to the conclusion that a gas could be relied upon almost to its boiling point. Thus helium furnishes the scale down to its boiling point (4·2°K). The corrections necessary to convert this scale to the thermodynamic scale may be obtained and have been given by Onnes and Cath. For temperatures below 4·2°K we must use the helium gas thermometer with the pressure well below the vapour pressure of liquid helium at the temperature to be measured, so that the gas will not liquefy at that temperature. With this device the helium gas thermometer gives us the thermodynamic scale down to 1°K. Now we shall consider the secondary standards.

Mercury freezes at −38·87 and alcohol at −111·8°C and hence these thermometers cannot be used below the respective temperatures. A special liquid thermometer containing fractionally distilled petroleum ether can be used down to −190°C.

But for all accurate work, however, *resistance thermometers* are employed. It is absolutely essential that the substance of which the thermometer is made is perfectly pure. Pure metals show a regular decrease in resistance with decrease of temperature. Dewar and Fleming found that the presence of the slightest trace of impurity in a metal is sufficient to produce a considerable increase in resistance at these low temperatures. It is, therefore, difficult to trust the purity of any specimen for very low temperatures without actual comparison. Henning found from a detailed investigation that the parabolic formula did not hold below −40°C. Van Dusen proposed the formula

$$t = \frac{R_t - R_0}{R_{100} - R_0}\,100 + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \epsilon\left(\frac{t}{100} - 1\right)\frac{t^3}{100^3}, \tag{10}$$

where ϵ is a constant and δ has already been defined on p. 14. The constants R_0, R_{100} and δ are determined by calibration at 0°C, 100°C and the boiling point of sulphur as explained previously, and the constant ϵ is then determined by calibration at the boiling point of oxygen (−182·97°C). Van Dusen's formula has been found to hold satisfactorily from 0°C to −190°C, the error nowhere being greater than ±0·05°.

For temperatures lower than −190°C, the platinum thermometer was used by Henning and Otto, and can be used with advantage up to 20°K. There is, however, no satisfactory formula for calculating the temperature from the observed resistance and a calibration curve has to be used. Sometimes lead and gold thermometers are also employed. Onnes has used lead down to −259°C and Nernst has given a method for calculating these temperatures. Below −250°C resistance thermometers of constantan and phosphor-bronze have been employed, the latter being much more sensitive.

For low temperatures copper-constantan and iron-constantan couples are very sensitive as they develop a large e.m.f. They can be used down to −255°C. They must be calibrated by direct comparison with a gas thermometer.

In order to measure temperatures below the temperature of boiling helium (−268°C) the vapour-pressure thermometer of helium can be employed. Its use is based on the well-known fact that the vapour pressure of a liquid varies uniquely with the temperature. Thus the method consists in measuring the vapour pressure of a liquid at the required temperature by means of an apparatus similar to that shown in Fig. 4, Chap. V, and obtaining the corresponding temperature by means of a calibration curve or a theoretical formula. The helium gas thermometer and the vapour pressure thermometer have been used down to about 0·75°K. For measuring still lower temperatures the paramagnetic susceptibility of salts is utilised.

18. International Temperature Scale.—We have seen that the thermodynamic centigrade scale is the standard scale of temperature and is given by the helium gas thermometer, but gas thermometry involves many experimental difficulties. On account of these difficulties in the practical realisation of the thermodynamic scale the International Committee in 1927 found it expedient to adopt a practical scale known as the International Temperature Scale. This scale agrees with the thermodynamic scale as closely as our present knowledge permits and is at the same time designed to be easily and accurately reproducible. It is based upon a number of reproducible fixed points to which numerical values have been assigned and the intermediate temperatures have been defined by agreement as the values given by the following thermometers according to the scheme given below :—

(1) *From 0°C to 660°C.*—The standard platinum resistance thermometer calibrated at 0°, 100°C and the boiling point of sulphur.

(2) *From −190°C to 0°C.*—The platinum resistance thermometer which gives temperature by means of the formula

$$R_t = R_0\{1 + \alpha t + \beta t^2 + \gamma(t-100)t^3\},$$

the four constants being determined by calibration at ice, steam, sulphur and oxygen points. It will be seen that this formula is equivalent to (10) where $\epsilon = (100)^2\ \delta\gamma/\beta$.

(3) *From 660°C to 1063° C.*—The platinum Pt-Rh thermocouple where temperature is defined by

$$E = a + bt + ct^2,$$

and the three constants are determined by calibration at the freezing point of antimony and at the silver and gold points.

(4) *Above 1063°C.*—An optical pyrometer (see Chap. XI) calibrated at the gold point (1063°C).

It should be emphasized that the International Scale does not replace the thermodynamic scale ; it merely serves to represent it in a practical manner with sufficient accuracy for most purposes.

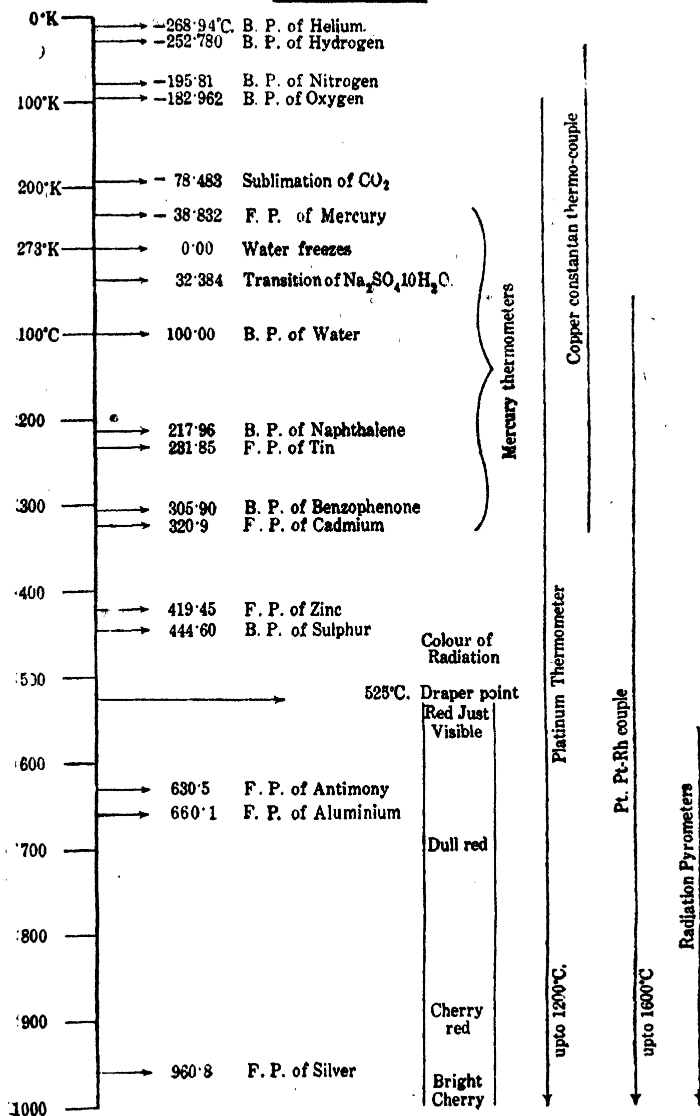
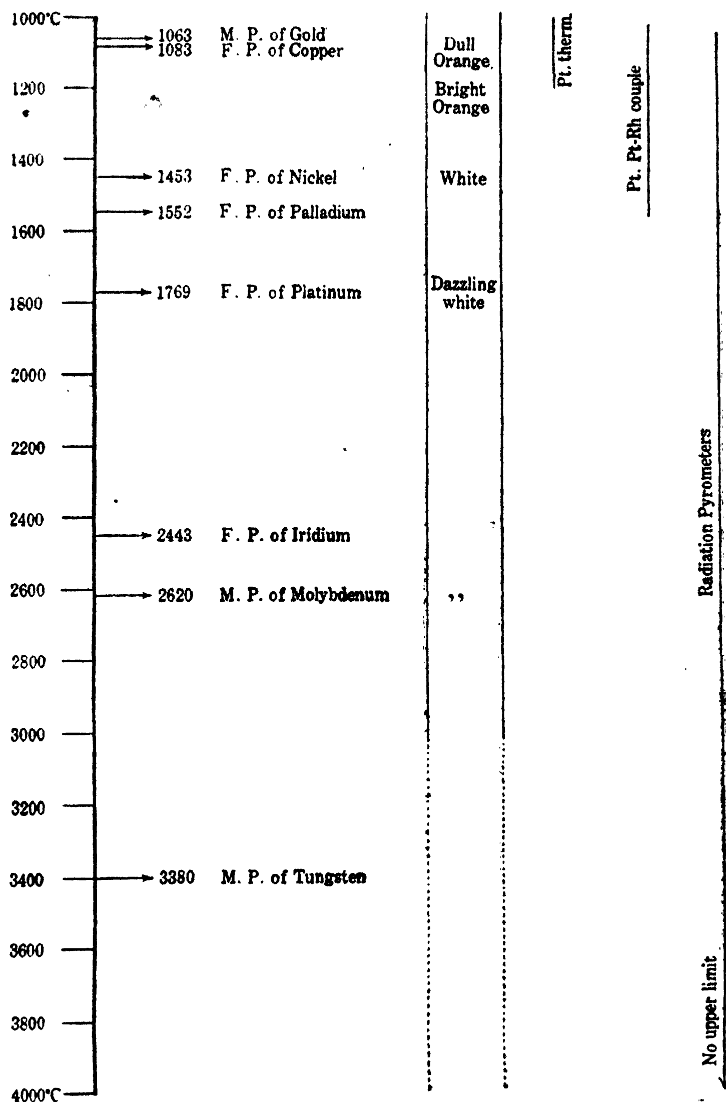
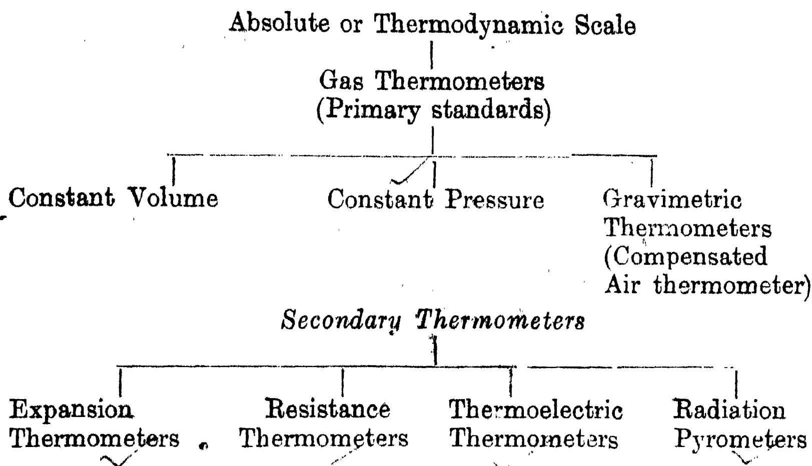

Chart of Fixed Points
0°K
100°K
200°K
273°K
100°C
200
300
400
500
600
700
800
900
1000
−268·94°C. B. P. of Helium.
−252·780 B. P. of Hydrogen
−195·81 B. P. of Nitrogen
−182·962 B. P. of Oxygen
− 78·483 Sublimation of CO_2
− 38·832 F. P. of Mercury
0·00 Water freezes
32·384 Transition of $Na_2SO_4 10H_2O$
100·00 B. P. of Water
217·96 B. P. of Naphthalene
231·85 F. P. of Tin
305·90 B. P. of Benzophenone
320·9 F. P. of Cadmium
419·45 F. P. of Zinc
444·60 B. P. of Sulphur
525°C. Draper point
630·5 F. P. of Antimony
660·1 F. P. of Aluminium
960·8 F. P. of Silver
Colour of Radiation
Red Just Visible
Dull red
Cherry red
Bright Cherry
Mercury thermometers
Copper constantan thermo-couple
Platinum Thermometer
upto 1200°C.
Pt. Pt-Rh couple
upto 1600°C
Radiation Pyrometers

Chart of Fixed Points (Contd).



19. Illustration of the Principles of Thermometry.



Books Recommended

1. Burgess and Le Chatelier, *The Measurement of High Temperatures.*
2. Ezer Griffiths, *Methods of Measuring Temperature*, (Griffin, 1947).
3. Henning, *Temperaturmessung.*
4. *A Dictionary of Applied Physics* (Glazebrook), Vol. I, Article on Thermometry.
5. J. A. Hall, *Fundamentals of Thermometry*, Institute of Physics, London (1953).
6. J. A. Hall, *Practical Thermometry*, Institute of Physics, London (1953).

Other References.

1. *Temperature, its Measurement and Control in Science and Industry* (1941), published by Reinhold Publishing Corporation, New York.

CHAPTER II

CALORIMETRY

1. Quantity of Heat.— It is a matter of common experience that when a hot body is placed in contact with a cold one, the former becomes colder and the latter warmer; we say that a certain quantity of heat has passed from the hot body to the cold one. But a simple experiment shows that when different bodies are raised to the same temperature and then allowed to exchange heat with a cold body the final temperature is different. If we take equal quantities of water in three different vessels at the same temperature and plunge equal masses of aluminium, lead and copper previously heated to 100°C into these vessels, one in each, the equilibrium temperature is highest for aluminium and least for lead. This indicates that, of these three metals, aluminium can yield the largest quantity of heat and lead the least.

For measuring quantities of heat we require a 'unit.' The quantity of heat required to raise the temperature of 1 gram of water through 1°C is called the '*calorie*' which is also the *thermal unit* for measuring quantities of heat. The 15°C *calorie* is defined as the quantity of heat which would raise the temperature of one gram of water from 14·5°C to 15·5°C and has been recommended by the International Union of Pure and Applied Physics (1934) for adoption as the standard. In Britain the *British thermal unit* (written B. Th. U.) is frequently employed* which represents the quantity of heat required to raise 1 lb. of water through 1°F. The *specific heat* of any substance is defined as the number of calories required to raise 1 gram of the substance through 1°C. This is strictly speaking not the same at all temperatures. Thus if a quantity of heat Q raises the temperature of m grams of a substance from θ to θ', s, the mean specific heat of the substance, is given by $Q/[m(\theta'-\theta]$; while if a quantity dQ raises the temperature by $d\theta$, the specific heat at the temperature θ is $\dfrac{dQ}{m \cdot d\theta}$.

The thermal capacity or *water equivalent* of a particular body is equal to the product of its mass and specific heat.

2. Methods in Calorimetry.—The following are the chief methods employed in Calorimetry† :—

(1) Method of Mixtures.
(2) Method of Cooling.

* Sometimes the lb. calorie or centigrade heat unit (C. H. U.) or centigrade thermal unit (C. Th. U.) is also used which represents the quantity of heat required to raise 1 lb. of water through 1°C.

† A good account of these methods is given in Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, article on "Calorimetry".

(3) Methods based on Change of State or Latent Heat Calorimetry.

(4) Electrical Methods.

In the following pages we shall discuss these methods one by one. Under each of these we shall consider the various forms of experimental arrangement that have been adopted. Solids and liquids will be considered first while gases will be taken up later in the chapter.

1. METHOD OF MIXTURES

3. Theory of the Method.—Regnault* about the year 1840 made a careful study of the Method of Mixtures, and by care and skill obtained results of the highest accuracy. The principle of the method is to impart the quantity of heat to be measured to a certain mass of water contained in a vessel of known thermal capacity and to measure the rise of temperature produced. Thus, if a substance of mass m_1, specific heat s_1 and initial temperature θ_1, be plunged into m_2 grams of water at temperature θ_2, and if W be the thermal capacity of the calorimeter, θ the final temperature of the mixture, we have, by equating the heat lost by the substance to the heat gained by the water and calorimeter,

$$m_1 s_1 \ (\theta_1 - \theta) = (m_2 + W) \ (\theta - \theta_2),$$

or

$$s_1 = \frac{(m_2 + W) \ (\theta - \theta_2)}{m_1(\theta_1 - \theta)}.$$

This gives the specific heat of the substance. Various corrections are, however, necessary for heat is lost by the system by conduction, convection and radiation. Thus for θ we must put $\theta + \triangle\theta$ where $\triangle\theta$ is the correction.

4. Radiation Correction.—In most experiments on calorimetry the calculation of this loss of heat due to radiation is important. The radiation correction may be accurately calculated with the help of Newton's Law of Cooling (Chap. XI) which states that for small differences of temperature the heat loss due to radiation is proportional to the temperature difference between the calorimeter and the surroundings. To illustrate its application let AB (Fig. 1) denote the observed rise of temperature during an experiment, BC the observed cooling at the end of it. We have to calculate the true rise in temperature. Divide the abscissa into n equal intervals δt_1, $\delta t_2, \ldots \delta t_n$ by means of ordinates P_1M_1, $P_2M_2, \ldots P_n M_n$ such that

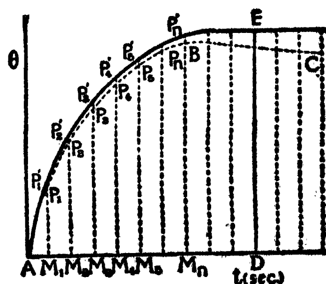


Fig. 1.—Illustration of Radiation Correction.

* Henri Victor Regnault (1810-1878), born at Aix-la-Chapelle, had to support himself while young. He joined the Ecole Polytechnique in Paris and later on in 1840 he was appointed Professor in that Polytechnique. He did many classic researches on heat.

the small portions AP_1, P_1P_2, ... $P_{n-1}P_n$, may be treated as straight lines. Let us measure temperatures from the temperature of the surroundings. If θ_1, θ_2...denote the mean temperatures during these intervals, θ_1', θ_2' . . . the temperatures at the ends of these intervals represented by P_1M_1, P_2M_2..., then the temperature diminution due to radiation in the interval δt_1 is $k\theta_1\delta t_1$. If θ_1'', θ_2'', . . . denote the temperatures at the ends of these intervals had there been no loss due to radiation, then

$$\theta_1'' = \theta_1' + k\theta_1\delta t_1 \qquad (1)$$

$$\theta_2'' = \theta_2' + k\theta_1\delta t_1 + k\theta_2\,\delta t_2 \qquad (2)$$

$$\therefore\quad \theta_n'' = \theta_n' + k(\theta_1\,\delta t_1 + \theta_2\delta t_2 + \ldots\ldots \theta_n\,\delta t_n)$$

$$= \theta_n' + k\ (\text{area of the curve } ABM_nA)$$

$$= \theta_n' + k\int_0^t \theta\ dt. \qquad (3)$$

We can thus correct any temperature θ_n' if we determine the area AP_nM_nA and k.

An alternative method is to plot the upper curve from the lower curve by increasing the ordinate M_1P_1 to M_1P_1', M_2P_2 to M_2P_2' etc. where $M_1P_1' = \theta_1''$, $M_2P_2' = \theta_2''$, etc. The highest ordinate on the curve (*viz.*, DE) gives the true rise of temperature in the experiment corrected for radiation.

To determine k we have to observe the rate of cooling at any temperature. The curve BC (Fig. 1) is obtained experimentally for this purpose. From this $\frac{d\theta}{dt}$ is calculated for any mean value of θ. Now $k = -\frac{1}{\theta}\frac{d\theta}{dt}$, hence k is known.*

Another method called the adiabatic method is to eliminate the heat by continuously adjusting the temperature of the bath enclosing the calorimeter to be always equal to the temperature of the calorimeter itself.†

5. Specific Heat of Solids.— For finding the specific heat of solids by this method the requisites are a calorimeter with an enclosure, a thermometer and a heater. For work at ordinary temperatures the calorimeter is made of thin copper, nickelplated and polished on the outside, so as to reduce radiation losses. It is supported on pointed pieces of wood or by means of thread inside a larger double-walled vessel which has water maintained at a fixed temperature in the

* A simple but rough method sometimes adopted is to add to the observed rise half the cooling observed at the highest temperature in a time equal to the duration of the experiment. This is based on the assumption that the average excess of temperature of the calorimeter over the surroundings may be taken to be half the final excess, hence the cooling during the experiment is half the cooling at the final temperature.

† For other methods see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, pp. 61-63.

annular space between the walls. The heater is a steam-jacket in which the substance is heated by steam without becoming wet. An oil bath may also be used. The transference and radiation errors must be reduced by suitable mechanical devices as in Regnault's classical experiments.

For high temperatures the solid substance is heated in an electric furnace. White in his work at high temperatures employed a furnace having a platinum coil wound on its surface. The substance is supported inside the furnace in a loop of platinum wire and is allowed to drop into the calorimeter by a suitable mechanical device. Change in temperature is measured by a resistance thermometer. For work at low temperatures the substance is cooled down in a quartz vacuum-vessel surrounded by liquid air before being dropped into the calorimeter.

Awbery and Ezer Griffiths have determined the specific heat of solids and molten liquids as well as their latent heat by using an improved apparatus based on the method of mixtures. This is discussed in Chap. V.

The use of water as calorimetric liquid has several drawbacks. Its range is small and specific heat large so that the rise of temperature is small; further there is considerable risk of some water being lost by evaporation. For these reasons several workers have replaced it by a block of metal. The copper block calorimeter devised by Nernst, Lindemann and Koref is exceedingly convenient for low temperatures. It consists of a heavy copper block K (Fig. 2) cemented with Wood's metal to the inside of a Dewer flask D. It is essentially a calorimeter based on the method of mixtures in which copper replaces water as the standard substance. The heated substance is dropped into the copper block through the glass-tube R and the change in temperature of the latter is read on thermo-couples T, T, whose one end is inside the copper block K and the other end in the block C. The copper block on account of its good conductivity keeps the temperature uniform. Jaeger and his co-workers have employed this method to determine the specific heat of W, Pt, Os, Rh, Ir, etc., to about 1600°C with a high degree of accuracy.

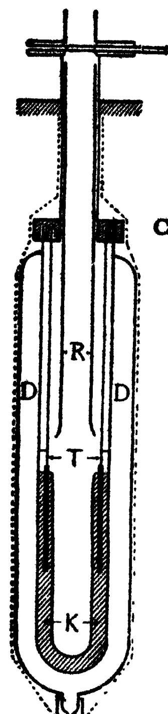


Fig. 2. Copper Block Calorimeter.

6. Specific Heat of Liquids.— Specific heat of liquids which do not react chemically with water or any other substance of known specific heat may be obtained by direct mixture. For liquids which react in this way Regnault used a different form of apparatus. The liquid was not allowed to mix with water but was admitted when desired into a vessel immersed in water. The liquid was first heated

and then forced into the vessel. The specific heat could be calculated as before.*

Another class of experiments for measuring the specific heat of liquids involves the expenditure of some mechanical energy and measurement of the consequent rise of temperature. To this class belong the classical experiments of Rowland for determining the mechanical equivalent of heat. They will be described in detail in Chapter III.

2. METHOD OF COOLING

7. This method, perfected by Dulong and Petit, is found to be most convenient for liquids but unsuitable for solids owing to variations of temperature within the latter. The method is based on the assumption that when a body cools in a given enclosure on account of radiation alone, the heat dQ emitted in the time dt is given by the relation

$$dQ = Af(\theta)dt, \qquad . \quad . \quad . \quad . \quad . \quad (4)$$

where A depends upon the area and the radiating power of the body, $f(\theta)$ is an unknown function of θ, the excess of the temperature of the body over that of the surroundings.

If this produces a cooling of the body through $-d\theta$, we have

$$dQ = -msd\theta,$$

where m and s denote the mass and the specific heat of the body respectively.

Equating these two expressions for dQ we get

$$-msd\theta = Af(\theta)dt.$$

Or

$$\int_0^t dt = -\frac{ms}{A}\int_{\theta_1}^{\theta_2}\frac{d\theta}{f(\theta)}$$

Or

$$t = \frac{ms}{A}\int_{\theta_2}^{\theta_1}\frac{d\theta}{f(\theta)}, \qquad . \quad . \quad . \quad . \quad . \quad (5)$$

where t is the time the body takes in cooling from $\theta_1°$ to $\theta_2°$.

Similarly for another substance to cool through the same interval of temperature

$$t' = \frac{m's'}{A'}\int_{\theta_2}^{\theta_1}\frac{d\theta}{f(\theta)}, \qquad . \quad . \quad . \quad . \quad (6)$$

If $A = A'$ *i.e.*, the surface area and the radiating power of the two bodies be the same we have from (5) and (6)

$$\frac{ms}{t} = \frac{m's'}{t'}. \qquad . \quad . \quad . \quad . \quad (7)$$

If masses m, m' of two liquids be contained successively in a calorimeter of thermal capacity W and the calorimeter suspended

* For details see Preston, *Theory of Heat.*

inside a vessel kept at 0°C by immersion in melting ice and then observations of the rate of cooling taken, we have

$$\frac{W+ms}{t}=\frac{W+m's'}{t'} \quad . \quad . \quad . \quad . \quad (8)$$

If one liquid is water ($s=1$), the specific heat of the other is thus determined from a knowledge of t, t', m, m'.

The method is sometimes employed for determining the specific heat of liquids but is not capable of any great accuracy and is mainly of historical interest.

3. METHODS BASED ON CHANGE OF STATE

8. These methods may be subdivided into two: namely the method of melting ice and the method of condensation of steam. These methods were of real advantage in the last century when accurate measurements of temperature were impossible, but with the recent development of accurate thermometers and electrical heaters they are now less in use, chiefly on account of their inherent defects. The second method is, however, very convenient for determining the specific heat of gases at constant volume and hence retains its importance.

*9. **Method of Melting Ice.**—In this method the heat given out by a certain substance in cooling is imparted to ice and measured by the amount of ice thereby melted. Thus if M grams of a substance of specific heat s and initial temperature θ are able to melt m grams of ice when placed in contact with the latter, the specific heat is given by the relation

$$Ms\theta = mL, \quad . \quad . \quad . \quad (9)$$

where L is the latent heat of fusion. The earliest forms of the apparatus as devised by Black, and by Lavoisier and Laplace were liable to cause considerable error. An improved form of the calorimeter was later devised by Bunsen* which will now be described.

*10. **Bunsen's Ice Calorimeter.**—In this calorimeter, the water produced by the melting of ice is not drained off but is allowed to remain mixed with ice and the resulting change in volume is observed. The calorimeter is illustrated in Fig. 3, p. 34. The test tube A is fused into the cylindrical glass bulb B which is provided with the glass stem C. B is nearly filled with boiled air-free water and the remaining space and the stem is filled with mercury. The stem terminates in an iron collar D containing mercury into which a graduated capillary tube E is pushed so that mercury stands at a certain graduation in E.

In conducting an experiment a stream of alcohol, cooled by a freezing mixture, is first passed through the test-tube A until a cap

* Robert Wilhelm Bunsen (1811-1899), born at Gottingen, studied at Gottingen, Paris, Berlin and Vienna. He was professor of Chemistry at Breslau and Heidelberg. His important researches are on spectrum analysis, Bunsen cell, grease-spot photometer, gas burner and ice calorimeter.

of ice F is formed round it in B. The whole instrument is then kept immersed in pure ice at 0°C for several days till all the water in B is frozen. It is then ready for use.

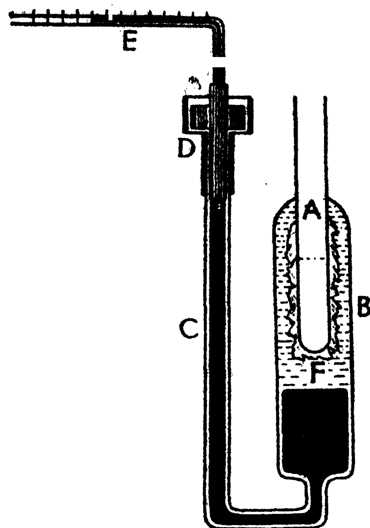


Fig. 3.—Bunsen's Ice Calorimeter.

To calibrate the scale on E, let a mass m of water at a temperature θ°C be poured into the test-tube. Some ice in B melts and the resulting contraction of mercury, say n divisions on E, is observed. Then if a recession of mercury by 1 division corresponds to q calories of heat

$$m\theta = nq \; ; \text{ or } q = m\theta/n. \quad (10)$$

Next the substance under investigation, previously heated to a temperature θ', is dropped into some water at 0° contained in the test-tube A. Then if M, s denote the mass and the specific heat of the substance respectively, and n' the observed recession of mercury thread in E, we have

$$Ms\theta' = n'q,$$

or

$$s = \frac{n'}{M\theta'} q = \frac{mn'\theta}{Mn\theta'} \quad . \quad . \quad . \quad . \quad (11)$$

This gives the specific heat of the substance. The specific heat of rare metals which can be had in small quantities can be readily found by this method. The apparatus is, however, not capable of great accuracy. A fundamental objection to the use of the ice calorimeter rests on the fact that a given specimen of water can freeze into ice of different densities.

11. Joly's Steam Calorimeter.—In the steam calorimeter devised by Prof. Joly in 1886 the heat necessary to raise the temperature of a substance from the ordinary temperature to the temperature of steam is measured by the amount of vapour condensed into water at the same temperature. It consists of a thin metal enclosure A (Fig. 4), double-walled and covered with cloth, which is placed beneath a sensitive balance. One pan of the balance is removed and from this end of the beam hangs freely a wire w supporting a platinum pan inside the enclosure. The substance whose specific heat is required is placed on this pan and weights added on the other pan till balance is attained. The temperature of the enclosure is observed by means of a thermometer inserted into the chamber, and in the meantime

steam is prepared in the boiler. It is then admitted suddenly into the chamber through the wide opening O at the top and can escape

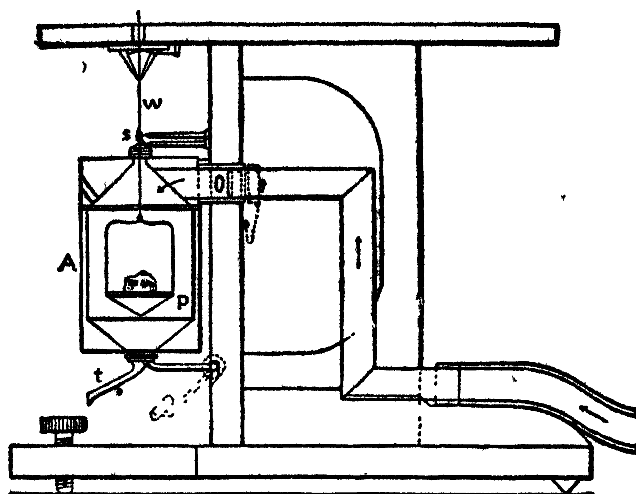


Fig. 4—Joly's Steam Calorimeter.

through the narrow exit-tube t at the bottom. Steam condenses on the substance and the pan, and weights are added on the other pan to maintain the equilibrium. When the pan ceases to increase in weight the readings are noted and the temperature of the steam read on a thermometer. During the final weighing the steam is allowed to enter the chamber through a narrow escape-tube so as not to disturb the pan. The weight becomes practically constant in four or five minutes though a very slow increase of about 4 milligrams per hour may be observed due to radiation. The difference between the two weighings gives the weight of steam condensed.

If W is the weight of the substance, w the increase in weight of the pan, θ_1 the initial temperature of the enclosure, θ_2 the temperature of steam, k the thermal capacity of the pan, L the latent heat of steam, s the required specific heat, then

$$Ws(\theta_2-\theta_1) + k(\theta_2-\theta_1) = wL. \quad . \quad . \quad . \quad (12)$$

k is determined from a preliminary experiment without any substance on the pan and thus the specific heat of the substance is found.

For great accuracy various precautions and corrections are necessary. Steam condenses on the suspending wire where it leaves the chamber and then surface tension renders accurate weighing difficult. A thin spiral of platinum wire in which a current flows, usually surrounds the suspending wire just above the opening, and is made to glow so that the heat developed is just sufficient to prevent condensation. A rapid introduction of steam is necessary in the early stages, for steam also condenses on the pan due to radiation to the cold air and the chamber, thus causing error. This is, of course, partially balanced by radiation from the steam to the substance later.

Further w does not accurately represent the weight of steam condensed since the first weight is taken in air at θ_1 °C and the second in steam at θ_2 °C. All the weighings must be reduced to vacuum and then the increase in weight calculated. Specific heat of rare substances can be found by this method since small quantities of the substance are needed but a sensitive balance is indispensable. The specific heat of liquids and powders can be found by enclosing them in glass or metal spheres whose thermal capacity is taken into account. Gases can also be similarly enclosed, but then the modified form of the apparatus—the differential calorimeter—is used.

12. The differential Steam Calorimeter.—In this form invented by Prof. Joly in 1889, both the balance pans are made exactly similar and of equal thermal capacity and hang in the same steam-chamber (Fig. 5). The substance to be tested is placed on one pan and the excess of steam condensing on this pan over that on the other pan is entirely due to the substance. Thermal capacity of the pans, radiation from them and all other sources of error common to them are eliminated, the substance bearing only its own share of the error. The chief use of this apparatus, however, consists in the determination of the specific heat of gases at constant volume. The pans are then replaced by two equal hollow spheres of copper furnished with "catch-waters" (shown in the figure). One sphere is filled with the dried experimental gas at any desired pressure while the other is empty. These spheres are counterpoised by adding necessary weights m which represent the mass of the contained gas. Steam is admitted and condenses on the pans. A larger amount of steam condenses on the sphere containing the gas, the excess, say w, giving the amount of steam required by the gas. Now the specific heat at constant volume c_v may be calculated from the equation

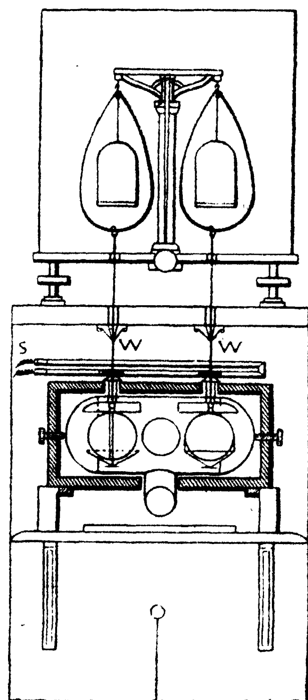


Fig. 5.—The differential Steam Calorimeter.

$$mc_v(\theta_2 - \theta_1) = wL, \qquad . \quad . \quad . \quad (13)$$

where θ_2, θ_1 are the final and initial temperatures of the chamber.

Prof. Joly used copper spheres of diameter 6·7 cm. and weighing 92·2 gm. and employed gases at different pressures. Corrections were applied for the following:—

1. The expansion of the sphere due to increased temperature and the consequent work done by the gas in expanding to this volume.

2. The expansion of the sphere due to the increased pressure of the gas at the higher temperature.

3. The thermal effect of this stretching of the material of which the sphere is made.

4. The increased buoyancy of the sphere due to its increased volume at the higher temperature.

5. The unequal thermal capacities of the spheres.

6. The reduction of the weight of water condensed to its weight in vacuum.

Dewar has devised calorimeters based on an analogous principle in which he employed a liquefied gas as the calorimetric substance. The heat to be measured is applied to the liquefied gas whereby the liquid evaporates absorbing its latent heat and the volume V of gas thus produced is measured. The heat communicated to the liquid is then given by $V\rho L$ where ρ is the density of the vapour and L the latent heat of vaporization of the substance. Using liquid oxygen and liquid hydrogen the apparatus can be adopted for very low temperatures. In the case of hydrogen 1 c.c. of vapour at N.T.P. corresponds to a very small quantity of heat (about 1/100 calorie). This method has been utilised for measuring the specific heat down to very low temperatures. The experimental substance (solid or liquid) is first kept in a constant temperature bath (say 0°C) and then dropped into the calorimeter containing liquid oxygen or liquid hydrogen.

4. ELECTRICAL METHODS

13. The electrical method was first employed by Joule in his attempts to determine the mechanical equivalent of heat. The electrical methods at present available may be subdivided into two:—

(1) Method based on the observation of rise of temperature.

(2) Method employing the steady-flow electric calorimeter.

We shall first consider the application of these methods to liquids because historically the method was first applied to them.

14. Methods Based on the Rise of Temperature.—Following Joule this method was adopted by many workers the chief among them being Griffiths, Schuster and Gannon, W. R. Bousfield and W. E. Bousfield. They employed this method for determining the mechanical equivalent of heat and found that it was capable of the highest accuracy. The same arrangements may be employed for finding the specific heat of liquids.

The principle of the method is to generate heat by passing a current through a conducting wire. If i is the current through the wire of resistance R and E the potential difference across its ends, the energy spent in a time t seconds is Eit ergs, provided E and i are expressed in electromagnetic units. If this raises the temperature of M grams of a substance by $\delta\theta°$, the specific heat s of the substance is given by the relation

$$Eit = JMs\,\delta\theta, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where J is the mechanical equivalent of heat (see Chap. III). If E

is expressed in volts and i in amperes the energy spent is given in Joules (1 Joule $=10^7$ ergs.).

Any two of the quantities E, i and R may be measured, thus giving three methods. Griffiths, in his determination of the specific heat of water, chose to measure E and R which is rather difficult for R must be measured during the heating experiment. Griffiths' work is important since it first established the fact that the electrical method can accurately give the value of J in absolute units. Schuster and Gannon measured E and i.

Jaeger and Steinwehr have applied this method to determine the mechanical equivalent of heat and hence also the specific heat at different temperatures. They employed a large mass of water (50 kg.) and consequently the thermal capacity of the vessel was only about 1% of that of the contained water. A section of their apparatus is shown in Fig. 6. AA is the cylindrical copper calorimeter lying on its side and properly insulated from the surrounding constant-temperature bath B. On the upper side at O there is a hole for the introduction of the heating coil H, the resistance thermometer and the shaft t which drives the stirrer SS. A current of about 10 amperes was allowed to flow for six minutes through the constantan heater H of 8 ohms resistance and the rise in temperature was about 1·4°C. In these experiments an accuracy of 1 in 10,000 was aimed at and hence the results are very reliable.

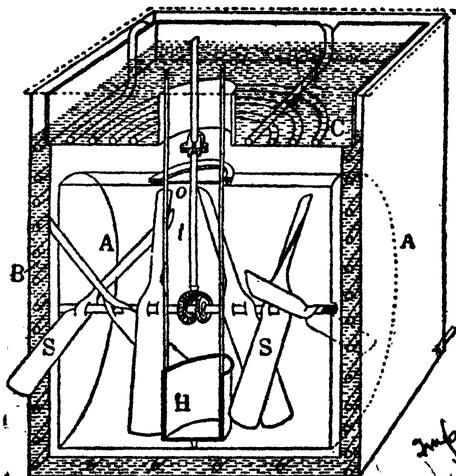
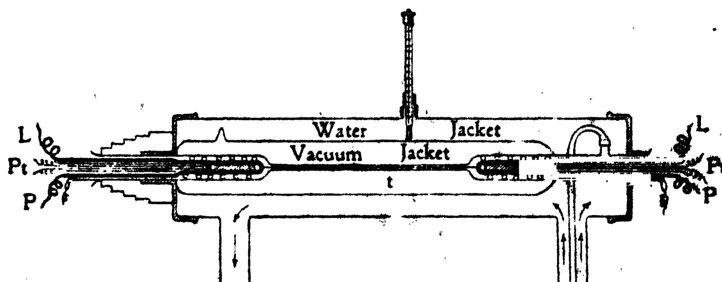


Fig. 6.—A Section of Jaeger and Steinwehr's Calorimeter.

15. The Method of Steady-flow Electric Calorimeter.—Great accuracy was attained by Callendar and Barnes by using the steady-flow electric calorimeter shown in Fig. 7. A steady current of the experimental liquid flowing through the narrow glass-tube t, about 2 mm. in diameter, is heated by an electric current flowing through the central conductor of platinum. The steady difference of temperature $\delta\theta$ between the inflowing and outflowing water is measured by a pair of platinum thermometers Pt, Pt at each end connected differentially in the opposite arms of a bridge of Callendar and Griffiths' type. The bulb of each thermometer is surrounded by a thick copper tube of negligible resistance attached to the central conductor. This on account of its good conductivity keeps the whole bulb at the temperature of the adjacent water, and due to its low resistance prevents the generation of any appreciable amount of heat by the

current near the thermometer. The leads L, L and P, P are attached to this tube of copper, the former for introducing the heating current and the latter for measuring the potential difference across the central conductor in terms of a standard cell by means of an accurately



•Fig. 7.—Steady-flow Electric Calorimeter.

calibrated potentiometer. The potentiometer also serves to measure the heating current i by measuring the potential difference across a standard resistance included in the same circuit. In order to diminish the external loss of heat the flow tube is enclosed in a hermetically sealed glass vacuum jacket surrounded by a constant temperature bath. Neglecting small corrections the general equation is

$$Eit = JMs\,(\theta_2-\theta_1)+Jht, \qquad (15)$$

employing the same notation as before, where h denotes the heat loss per second on account of radiation, and θ_1, θ_2 the temperatures of inflowing and outflowing water. The time of flow t in these experiments was about 20 minutes and was recorded automatically on an electric chronograph reading to 0·01 sec. The mass of water M was measured by collecting the outflowing water and was about 500 gm. The difference in temperature $\theta_2-\theta_1$ was from 8° to 10°C and was accurately read to ·001°C. The heat loss h was very small and regular, and was determined and eliminated by suitably adjusting the electric current so as to secure the same rise of temperature for different rates of flow of the liquid. Thus for two rates of flow we have

$$E_1i_1t = JM_1s(\theta_2-\theta_1) + Jht,$$

$$E_2i_2t = JM_2s(\theta_2-\theta_1) + Jht,$$

$$\therefore \quad J = \frac{(E_1i_1-E_2i_2)t}{(M_1-M_2)\ (\theta_2-\theta_1)s}.$$

Since the temperatures at every point of the apparatus are the same in both experiments the heat loss h must also be the same. The specific heat s thus determined is the average specific heat for the interval $\delta\theta$ and may be taken as the specific heat at the middle of the interval.

The great advantage of this steady-flow electric method is that no correction is necessary for the thermal capacity of the calorimeter

since there is no change of temperature in any part of the instrument. Care must, however, be taken to secure perfect steadiness, as it is practically impossible to correct for unsteady conditions. Further, since all conditions are steady, the observations can be taken with the highest degree of accuracy. There is no question of thermometric lag. It is essential, however, that the current of water be thoroughly mixed otherwise temperature over a cross-section of the tube will not be uniform. This is secured by having the central conductor in the form of a spiral instead of a straight wire.

Callendar and Barnes used this method to find the specific heat of water at various temperatures. Their results are discussed in the next section. Callendar found the specific heat of mercury by this method. The central conducting wire was dispensed with, the flowing mercury itself serving as the conductor. Griffiths employed this method to determine the specific heat of aniline over the range 15° to 50°C.

16. Specific Heat of Water.—In ordinary calorimetric experiments the specific heat of water is assumed constant at all temperatures and equal to unity. Accurate investigations of the last section, show that it varies with temperature. The first accurate experiments in this connection were those of Rowland in connection with his determination of the mechanical equivalent of heat (Chap. III). He argued that if the specific heat of water at all temperatures were constant this mechanical equivalent must come out a constant quantity even if we used water at different temperatures. The variation in the value of J was due to the variation in specific heat.

Table 1.—Specific Heat of Water at different temperatures.

Temp. °C.	Callendar & Barnes	Jaeger and Steinwehr	Osborne Stimson & Ginnings	Specific heat in int. Joules (O, S. & G)
0	1·0093	(1·005)	1·0076	4·2169
5	1·0047	1·0029	1·0039	4·2014
10	1·0019	1·0013	1·0015	4·1914
15	1·0000	1·0000	1·0000	4·1850
20	0·9988	0·9990	0·9991	4·1811
25	0·9980	0·9983	0·9985	4·1788
30	0·9976	0·9979	0·9982	4·1777
35	0·9973	0·9978	0·9982	4·1774
40	0·9973	0·9981	0·9983	4·1778
45	0·9975	0·9987	0·9985	4·1787
50	0·9978	0·9996	0·9988	4·1799
60	0·9987		0·9997	4·1836
70	1·0000		1·0009	4·1888
80	1·0017		1·0025	4·1956
90	1·0036		1·0046	4·2043
100	1·0057		1·0072	4·2152

The other accurate experiments on the subject are those of Callendar and Barnes (sec. 15) and of Jaeger and Steinwehr (sec. 14). Both of them determined accurately the specific heat of water at various temperatures. Their values are given in Table 1 together with the values obtained recently by Osborne, Stimson and Ginnings at the National Bureau of Standards, Washington. In column 5 the specific heat is expressed in international Joules* per gram per °C.

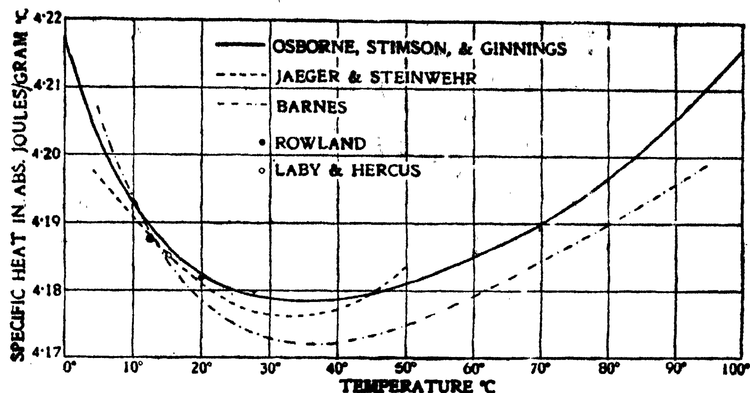


Fig. 8.—Specific Heat Curve for Water.

The results of all these three investigations are plotted in Fig. 8. It will be seen that the values obtained by Callendar and Barnes lie somewhat wide of the others and appear to be less reliable chiefly on account of the uncertainty in the values of the electrical units employed. From these curves it is evident that water has a minimum specific heat at about 34°C. It is on account of this variation that on p. 28 the calorie was defined with respect to 15°C.

Specific Heat of Solids

17. Rise of Temperature Method.—The electrical method was first applied to solids by Gaede in 1902. E. H. Griffiths and E. Griffiths determined the specific heat of many metals over the range −160° to +100°C. The substance was used in the form of a calorimeter and was first cooled below the desired temperature. Electrical energy was utilised in heating the calorimeter and the temperature indicated by a resistance thermometer. The calorimeter was enclosed in a constant temperature bath whose temperature was kept constant to 1/100th of a degree. Correction was applied for the heat lost by radiation.

18. Nernst Vacuum Calorimeter.— A different form of the apparatus, known as the *vacuum calorimeter*, was used by Nernst and Lindemann for measuring the specific heat at very low temperatures. This differed from Gaede's form essentially in having the calorimeter suspended in *vacuum*. The results achieved with its aid are of great theoretical importance and hence their apparatus will be considered

* 1 Int. Joule = $1{\cdot}00041 \times 10^7$ ergs.

in some detail. For good conducting solids such as metals the calorimeter shown in Fig. 9(a) was used. The substance whose specific heat is to be determined is shaped into a cylinder C, having a cylindrical hole drilled almost through its entire length, and a closely fitting plug P made for it from the same material. The substance here acts as its own calorimeter. The plug is wound over with a

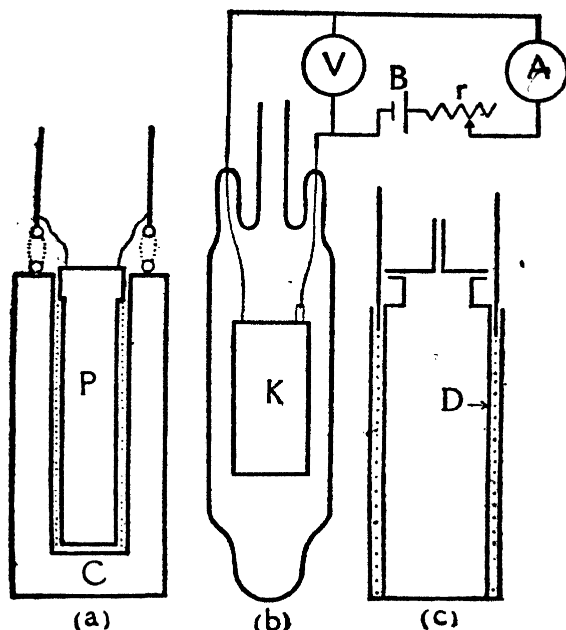


Fig. 9.—Nernst Vacuum Calorimeter.

spiral wire of purest platinum (shown dotted in the figure) which is insulated from it by means of thin paraffined paper, and finally liquid paraffin is poured over it. The upper part of the plug is somewhat thicker than the lower part, thus a good thermal contact is obtained. The calorimeter K thus constructed is suspended inside a pear-shaped glass bulb [shown at(b)] which can be filled with any gas or evacuated. The whole can be surrounded by suitable low temperature baths such as liquid air or liquid hydrogen. The platinum spiral, which serves both as electric heater and resistance thermometer, is connected in series with the battery B, resistance r and a precision ammeter A, the voltmeter V indicating the potential difference across the spiral. In order to bring the calorimeter to the desired temperature of experiment, hydrogen which is a good conductor of heat was first admitted into the pear-shaped vessel and the latter surrounded by a suitable bath. Next the vessel was completely evacuated so that the heat losses from conduction and radiation were almost entirely eliminated. In addition it was surrounded by liquid air or liquid hydrogen.

To carry out an experiment a current was allowed to flow through the heater for t seconds and the voltage across it was adjusted to be constant by varying the resistance r. If R_f, R_i and i_f, i_i denote the final and initial values of the resistance of the heater and the current through it respectively and E the constant potential difference,

$$R_f = \frac{E}{i_f}\ ;\ R_i = \frac{E}{i_i} \quad . \quad . \quad . \quad . \quad (16)$$

Thus an observation of i_f, i_i and E gives R_f and R_i, and from a previous determination of the resistance of the platinum spiral at various temperatures the rise in temperature $\delta\theta$ can be found. The energy supplied electrically is Eit where i is the average value of the current. Now if M is the mass of the substance forming the calorimeter, s its specific heat, we have,

$$Eit = JMs\,\delta\theta + h. \quad . \quad . \quad . \quad . \quad (15)$$

This gives the specific heat at a single temperature since $\delta\theta$ is usually 1° or 2°. The heat capacity of the paper and paraffin can be found and eliminated by taking different amounts of the substance and at the same time arranging that the temperature rise is the same. The heat loss h is very small and is determined and accounted for by observing the rate of cooling before and after the experiment.

For *non-conducting* solids the calorimeter shown in Fig. 9 (c) was employed. The heating wire was wound over a cylindrical silver vessel D and the whole covered with silver foil to diminish heat loss. This foil was soldered at the bottom of the cylinder as indicated. The solid whose specific heat is required was placed inside the silver cylinder and the latter closed with the lid. The silver on account of its high conductivity keeps the temperature uniform and this is further secured by filling the cylinder with air through the tube in the lid. The tube is then closed with a drop of solder so that it may be gas-tight. It is absolutely necessary that air should be present inside the vessel to facilitate equalisation of temperature throughout the experimental substance. Liquids and gases can be similarly admitted into the cylinder and their specific heat determined.

19. Results of Early Experiments.—In 1819 Dulong* and Petit from their investigations concluded that the *product of atomic weight and specific heat was constant for many substances*, or in other words, *atoms of all substances have the same capacity for heat*. Regnault from his own researches found that for ordinary substances the mean value of the constant was 6·38 with extremes of 6·76 and 5·7. A more accurate value of the constant can be obtained from the kinetic theory (Chap. III). The atomic heat at constant volume is shown there to be equal to $3R = 5{\cdot}955$. According to Richarz, the value of the ratio c_p/c_v for many substances lies between 1·01 and 1·04, hence the atomic heat at constant pressure, the quantity commonly determined should lie between 6·01 and 6·19. This law is of great

* Pierre Louis Dulong (1785-1838), a distinguished French scientist who lost an eye and a finger owing to the explosion of some nitrogen chloride which he discovered.

use in determining atomic weights. In illustration of the law table* 2 is added.

Table 2.—Illustration of Dulong and Petit's law.

Element		Atomic Weight (1)	Mean specific heat (2)	Atomic heat (1) × (2)
Sodium	..	23·00	0·307	7·06
Magnesium	...	24·32	0·247	6·00
Aluminium	...	27·1	0·2175	5·83
Iron	...	55·84	0·110	6·14
Nickel	...	58·68	0·1092	6·41
Copper	...	63·57	0·0930	5·92
Zinc	...	65·37	0·0939	6·14
Silver	...	107·9	0·0559	6·03
Cadmium		112·4	0·0557	6·26
Tin	..	118·7	0·0556	6·60
Antimony	...	121·8	0·0502	6·10
Platinum	...	195·2	0·0318	6·21
Gold	...	197·2	0·0309	6·10
Lead	..	207·2	0·0310	6·43
Bismuth	..	209·0	0·0299	6·22

Mean value = 6·24

In 1831 Neumann enunciated a similar law concerning molecular heats: *the product of the specific heat and the molecular weight of compounds of similar composition is nearly constant.* The value of the constant varies from one series of compounds to another. In illustration of the law table† 3 is added.

Table 3.—Molecular Heat of Oxides.

Compound		Specific heat (1)	Molecular weight (2)	Molecular heat (1) × (2)
Fe_2O_3	...	0·1700	159·8	27·2
Cr_2O_3	..	0·1796	192·0	27·4
As_2O_3	...	0·1277	197·8	25·3
Sb_2O_3	...	0·0901	287·8	25·9
Bi_2O_3	...	0·0605	464·8	28·1

Mean value = 26·8

* Taken from *Handbuch der Experimental-Physik*, Vol. 8, p. 193.
† Taken from *Handbuch der Experimental-Physik*, Vol. 8, p. 200.

Neumann's law can be considered as a particular case of the following law: The molecular heat of a compound may be considered as the sum of the atomic heats of its constituents. Thus if a compound has the composition $A_a B_b C_c D_d$ its molecular heat C_p is given by the relation

$$C_p = aC_{pA} + bC_{pB} + cC_{pC} + dC_{pD}. \quad . \quad . \quad (17)$$

where A, B, C, D stand for the different types of atoms composing the compound and C_{pA}, C_{pB}, etc., their atomic heats given by Dulong and Petit's law. The law is of much use in evaluating the molecular heats of certain substances.

20. Variation of Specific Heat with Temperature.—The specific heat as determined by the foregoing methods is not found to be a constant quantity. For solids and liquids pressure has little or no effect on specific heat. Rise of temperature, however, in general produces an increase in the specific heat. The specific heat at very low temperatures shows a marked decrease. To illustrate this table 4 is appended.

Table 4.—Atomic heat of silver at different temperatures.

Temp. in °K.	Atomic heat	Temp. in °K.	Atomic heat
1·35	0·000254	55·88	3·186
5	0·00509	74·56	4·039
10	0·0475	103·14	4·797
20	0·3995	144·38	5·373
36·16	1·694	205·3	5·605

These variations have been successfully accounted for by the quantum theory of specific heats. The earlier observations are accounted for by the kinetic theory (Chap. III).

21. Two Specific Heats of a Gas.—The specific heat of a gas, as of solids and liquids, may be defined as the ratio of the heat absorbed to the rise in temperature, taking a unit mass of the gas. A little consideration will show that this definition requires to be restricted. Imagine a quantity of gas to be suddenly compressed. The temperature of the gas will be found to rise, though no heat has been added. The ratio, *heat added/increase in temperature i.e.* specific heat, vanishes. Again let this compressed air expand suddenly ; a cooling would take place. This is just prevented by applying some heat to the gas. In this case the ratio, *heat added/change in temperature* becomes infinite. Thus we see that the original definition gives an infinite range of values for the specific heat. Hence external conditions are of paramount importance in determining the specific heat of gases. It has become customary to speak of two specific heats of a gas: the specific heat at constant volume denoted by C_v and the specific heat at constant pressure

denoted by C_p. In the former process the gas is maintained at constant volume so that the whole heat applied goes to increase the internal energy of the gas. In the latter case the gas is allowed to expand against a constant pressure and in so doing it does external work. This work is obtained by using up part of the heat energy applied to the gas. Hence the specific heat at constant pressure is necessarily greater than the specific heat at constant volume by an amount which is simply equal to the thermal equivalent of the work done by the gas.

Let us assume that the gas is perfect, *i.e.*, its molecules exert no influence on one another. This is approximately true for the permanent gases as Joule's experiment (Sec. 22) shows. Hence in this expansion no internal work against molecular attractions is done by the gas and the excess of heat supplied in the second case is simply the thermal equivalent of the external work. Consider the gas enclosed in a vessel of any shape and suppose the walls of the vessel can expand outwards. Let δA denote an element of area of the walls and δx the distance traversed by it measured along its outward drawn normal. Then the work done by the gas in this expansion against a constant external pressure p is $p\,\delta A\delta x$ and for the expansion of the entire surface the work is equal to $\Sigma\, p\delta A.\delta x = p\Sigma\,\delta A.\delta x = p\delta V$ where δV is the increase in the volume of the gas. Suppose a gramme-molecule of the gas, occupying a volume V_1 at temperature T°K and pressure p, expands to a volume V_2 at temperature $(T+1)$°K, the pressure remaining constant. Let $Mc_p = C_p$, $Mc_v = C_v$ where M is the molecular weight of the gas. C_p and C_v may be called gram-molecular or molar specific heats. The work done by the gas in expanding from V_1 to V_2 is

$$p(V_2-V_1) = R[(T+1)-T] = R, \quad . \quad . \quad . \quad (18)$$

by the gas laws. The thermal equivalent* of this work is $J(C_p-C_v)$. Hence

$$J(C_p-C_v) = R\dagger. \quad . \quad . \quad . \quad . \quad (19)$$

Or, if either R is expressed in calories, or C_p and C_v measured in ergs we get

$$C_p - C_v = R.$$

This relation was first deduced by R. Mayer.

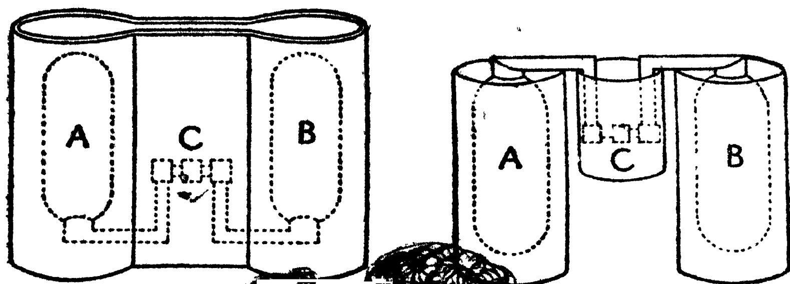
22. Experiments of Gay-Lussac‡ and Joule.—Gay-Lussac first carried out experiments to determine whether a gas does any internal

* This assumes the First Law of Thermodynamics which will be discussed in Chapters III and X.

† This is true for a perfect gas only. For real gases it can be shown that $C_p-C_v=T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$ where the differentials must be evaluated from the actual equation of state (Chapter IV) for the gas.

‡ Louis Joseph Gay-Lussac (1778-1850) was a distinguished French scientist who investigated on the expansion of gases. He was interested in aviation and in 1804 made a balloon ascent for the purpose of making experiments. He was created a peer of France.

work in expanding. He allowed gas contained in a vessel at a high pressure to expand into an evacuated vessel and observed the fall of temperature in one and the rise of temperature in the other vessel. This is called *free expansion* or *Joule expansion*. In this the gas as a whole does no external work while its volume increases, and the only work done will be that against molecular attractions which is called internal work. Somewhat later Joule employed a similar apparatus but he immersed the vessel in calorimeters. His apparatus



Joule's experim[illegible] one calori[illegible] Fig 1[illegible]

[illegible]e's experiment with two calorimeters. Fig. 11

is indicated in Figs. 10 and 11. The two vessels A and B communicated with each other through a tube furnished with a stop-cock C. A was filled with dry air at 22 atmospheres while B was exhausted. First the whole apparatus was placed in a single calorimeter (Fig. 10) and the stop-cock C opened. No change in temperature of the water was observed showing that no internal work against molecular attractions was done by the gas in expanding. To investigate the point further, the parts A, B, C were placed in separate vessels (Fig. 11), containing water whose temperature could be read by sensitive thermometers. On opening the stop-cock C the air expanded into B and the temperature of the vessel surrounding A fell while the temperatures of B and C rose. It was found that the heat lost by A was exactly equal to the sum of the heats gained by B and C, thus the total change in the internal energy of the gas during expansion is zero, *i.e.*, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ where U is the internal energy and V the volume. This is called *Joule's law* or *Mayer's hypothesis*. This shows clearly that no internal work is done by a gas in expanding. Joule's law holds only for the perfect gas to which the permanent gases of Nature like helium, hydrogen, etc. approximate. For further discussion see Chap. VI, sec. 16 and Chap. X, sec. 3. As a matter of fact, a slight fall in temperature should be observable in Joule's experiment with one calorimeter but on account of the large heat capacity of the calorimeter it escaped detection.

23. Adiabatic Transformations.—When the pressure and volume of a substance change but no heat is allowed to enter or leave it, the transformations are said to be adiabatic (a=not, dia=through, bates=heat, *i.e.*, heat not passing through). In an isothermal change the temperature is kept constant by adding heat to or taking it away from the substance. Consider an amount of heat δQ applied to a perfect gas. This is spent in raising the temperature of the gas and in doing external work. If we consider a gramme molecule of the gas, the former is equal to $C_v dT$ and the latter equal to pdV/J, both in calories. Hence

$$\delta Q = C_v dT + pdV/J,$$

or, if δQ and C_v are measured in ergs,

$$\delta Q = C_v dT + pdV. \quad . \quad . \quad . \quad . \quad (20)$$

This equation combined with $pV = RT$ will give the solution of all problems on perfect gases.* In an adiabatic transformation $\delta Q = 0$. Therefore

$$C_v dT + pdV = 0. \quad . \quad . \quad . \quad . \quad (21)$$

In order to find a relation between p and V we must eliminate T from (21) by means of the gas equation $pV = RT$. Differentiating the latter, we have,

$$pdV + Vdp = RdT. \quad . \quad . \quad . \quad . \quad (22)$$

Substituting for dT from (22) in (21), we get

$$C_v \frac{pdV + Vdp}{R} + pdV = 0.$$

and replacing R by $C_p - C_v$,

$$C_v Vdp + C_p pdV = 0.$$

Denoting C_p/C_v by γ we obtain

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0,$$

which on integration yields

$$\log p + \gamma \log V = \text{constant},$$

or

$$pV^{\gamma} = \text{constant}. \quad . \quad . \quad . \quad . \quad (23)$$

This is the adiabatic relation between p and V for a perfect gas.

To find the adiabatic relation between T and V or between T and p we must respectively eliminate p or V between equation (23) and the gas equation $pV = RT$. The results are

$$TV^{\gamma-1} = \text{constant}, \quad . \quad . \quad . \quad . \quad (24)$$

$$Tp^{(1-\gamma)/\gamma} = \text{constant}. \quad . \quad . \quad . \quad . \quad (25)$$

Exercise.—Dry air enclosed at 25°C and at atmospheric pressure is suddenly compressed to half its volume. Find (*a*) the resulting temperature, (*b*) the resulting pressure. Assume $\gamma = 1{\cdot}40$.

* For real gases instead of $PV = RT$, and $C_p - C_v = R$, we must substitute the actual equation of state and the true value of $C_p - C_v$. We shall then get the relation between p, V and γ for real gases.

(*a*) From (24) $T_1 = T(V/V_1)^{\gamma-1} = (273+25)\ (2)^{1\cdot4-1} = 393°K.$

(*b*) From (23), $p_1 = p(V/V_1)^{\gamma} = p \times 2^{1\cdot4} = 2\cdot64$ atm.

24. Experimental Methods*.— Let us now consider the experimental methods of finding the specific heat of gases. Since for perfect gases $C_p - C_v = R$, a knowledge of one of the specific heats gives the other. Again, if we determine γ, *i.e.*, C_p/C_v, the above relation will give both C_p and C_v. Hence the experimental methods may be divided into three classes:

(*a*) The measurement of C_p

(*b*) The measurement of C_v

(*c*) The determination of γ.

(*a*) MEASUREMENT OF C_p

25. The specific heat at constant pressure has been found either by the Method of Mixtures or by the Constant-Flow Method. The principles of these methods have already been explained.

26. Method of Mixtures—Regnault's Apparatus. The method was first applied to gases by Lavoisier and Laplace. Improvements

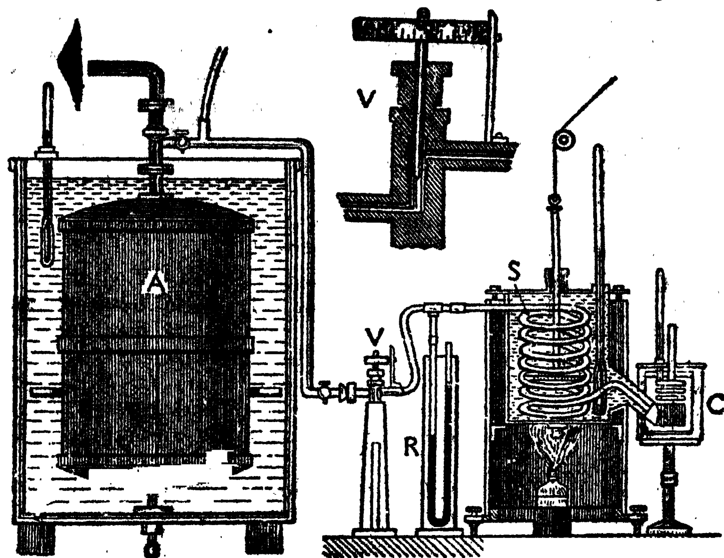


Fig. 12.—Regnault's Apparatus for C_p.

were made later by Delaroche and Berard, Haycroft and Regnault. Regnault with his great experimental skill obtained results of high accuracy. His apparatus is indicated in Fig. 12. Pure dry gas was

* The reader will find a very good account of these methods in Partington and Shilling: *Specific Heat of Gases.*

compressed in the reservoir A which was immersed in a thermostat. The reservoir was provided with a manometer (not shown). Gas could be allowed to flow through the stop-cock V at a uniform rate. This was effected by continuously adjusting the stop-cock V (shown separately) so that the pressure indicated by the manometer R was constant. The gas then flowed through a spiral S immersed in a hot oil-bath and then into the calorimeter C finally escaping into the air. The gas acquired the temperature T of the bath and raised the temperature of the calorimeter, say, from θ_1 to θ_2.

If m is the mass of the gas that flows into the calorimeter, c_p its specific heat is given by

$$mc_p\left(T-\frac{\theta_1+\theta_2}{2}\right)=w(\theta_2-\theta_1), \quad . \quad . \quad (26)$$

where w is the thermal capacity of the calorimeter and its contents. The mass m of the gas was determined by Regnault as follows:— for any pressure p he assumed that the weight W of the gas contained in the reservoir at temperature θ was given by the relation

$$W(1+\alpha\theta) = Ap+Bp^2+Cp^3$$

where A, B, C were determined from a series of preliminary experiments. Hence the weight W' of gas corresponding to the observed pressure p' at the end of the experiment is given by

$$W'(1+\alpha\theta) = Ap'+Bp'^2+Cp'^3$$

Thus $W-W'$, *i.e.*, the weight of the gas that flowed out was found.* In practice, corrections are necessary for the loss or gain of heat by conduction, convection and radiation which have to be found out by observing the change in temperature of the calorimeter before and after the experiment, and taking the average.

27. Other Experiments. The experiments of Wiedemann were essentially similar to those of Regnault. Lussana devised a high-pressure apparatus in which the same amount of gas enclosed at a high pressure can be repeatedly heated and passed through the calorimeter. The principle employed is the same as in Regnault's experiment. This apparatus can be used to find the specific heat of gases at very high pressure and possesses the advantage that the gas is not wasted.

For determining the specific heat at high temperatures the experiment of Holborn and Henning may be mentioned. Employing suitable electric heaters, resistance thermometers and well-designed calorimeter they were able to find the specific heats of nitrogen, carbon dioxide and steam up to 1400°C. The calorimeter corrections are

* If the perfect gas relation $pv=RT/M$ (p. 5), where v is the specific volume of the gas and M its molecular weight, is assumed to hold, a simpler expression for $W-W'$ can be easily obtained. Let V denote the volume of the reservoir and $\rho = 1/v$, the density of the gas. Then

$$W = V\rho = \frac{VpM}{RT}, \text{ and } W-W' = \frac{VM}{RT}(p-p'),$$

where p is expressed in dynes and R in ergs.

difficult and uncertain. The same method has been used by Nernst in finding the specific heat of ammonia up to 600°C.

28. Constant-flow Method. For finding the variation of specific heat with temperature the constant-flow method is most suitable, and was first used by Swan. The most recent form of the apparatus is that used by Scheel and Heuse in finding the specific heat down to very low temperature and is in principle similar to that shown in Fig 7.

The gas under test, previously brought to a steady temperature by passing through a suitable bath, flows through the calorimeter in a steady stream. Inside the calorimeter it is heated electrically by a heating coil of constantan and thus the energy supplied can be calculated. The temperatures of the incoming and outgoing gases are observed by resistance thermometers. The specific heat can be calculated by an equation similar to (15).

For work at low temperatures the gas was initially passed through a low temperature bath in which the calorimeter was also immersed. In studying helium and other rare gases Scheel and Heuse modified the apparatus so as to employ a closed circuit. These experimenters carried out measurements on various gases in the range 0° to −180°C.

For measurement of specific heat at high pressure the constant-flow method has been employed by Holborn and Jakob and gives the most reliable results.

(b) METHODS BASED ON THE MEASUREMENT OF C_v

29. Steam Calorimeter. The direct determination of C_v is best made by means of Joly's steam calorimeter (sec. 12). The method of carrying out the experiment and the necessary details will be found in that section.

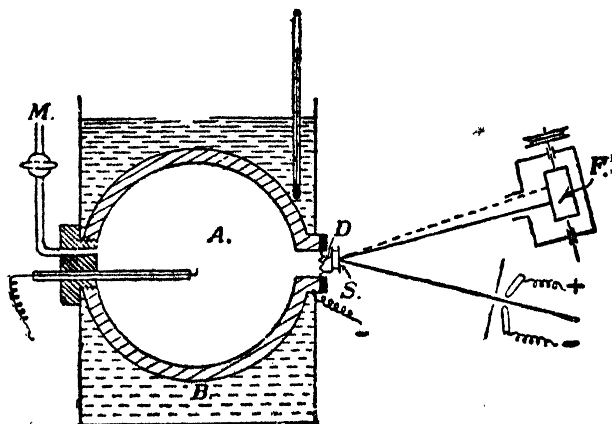


Fig. 13.—Pier's Explosion Bomb.

30. Explosion Method. Following the work of Bunsen, Vieille and others, Pier improved the explosion method and devised the

modern explosion bomb indicated in Fig. 13. Immersed in the water-bath B is a steel-bomb A which has a side-tube M through which the bomb can be evacuated and various gases introduced at the desired partial pressures. S is a corrugated steel membrane closing an opening in the bomb and carrying a mirror S. Light reflected from the mirror falls on the photographic film F which revolves on a drum. By applying various known static pressures and noting the deflection of the light spot, the pressure attained in any experiment can be found simply from the record on the film. Any explosion mixture, say, a mixture of hydrogen and oxygen together with the inert gas whose specific heat is required, is introduced in the bomb. By 'inert' is meant any gas which will not take part in the reaction either from want of chemical affinity or due to its presence in excess. The partial pressures of the various gases are known. The explosion is started by means of electric sparks and the final pressure reached (p_1) is observed. This takes about ·01 sec.

The calculation may be easily made. If the vessel were allowed to cool to the initial temperature T_2 (absolute), suppose it would record the pressure p_2. The maximum temperature T_1 reached during the explosion is calculated from the value of p_1, for, from the gas laws, since the volume remains constant,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}. \quad \therefore \quad T_1 = \frac{p_1}{p_2} T_2 .$$

Or if p_i denote the initial pressure and e the ratio of the final to the initial number of molecules (owing to the explosion the total number of molecules changes),

$$p_2 = ep_i \quad [\because \text{ volume and temperature are the same}]$$

$$\therefore \quad T_1 = \frac{p_1}{ep_i} \cdot T_2 = \frac{P}{e} T_2, \qquad . \quad . \quad . \quad . \quad . \quad (28)$$

where P is the ratio of explosion pressure to initial pressure. The relation connecting the specific heats and the heat of reaction is

$$mQ_2 = (T_1 - T_2) \; [mC_{vr} + nC_{vi}], \qquad . \quad . \quad . \quad (29)$$

where m is the number of gramme-molecules of the reaction products; n the number of gramme-molecules of the inert gas; C_{vr}, C_{vi}, respectively their mean molar specific heats over the range $(T_1 - T_2)$, and Q_2 the heat of reaction for the explosion mixture at T_2°. Q_2 is generally known from thermo-chemical data. We can determine C_{vr} by exploding either with different amounts of a gas whose variation of specific heat with temperature is known, or with different quantities of argon, a substance whose specific heat is constant. Then the same reacting gases may be exploded with any inert gas, and knowing C_{vr}, we can find C_{vi} for the inert gas.

The method is very suitable for measurements of specific heat at high temperatures and has been used to about 3000°C but suffers from the disadvantage that directly it gives only the average values over a wide range and not the specific heat at any temperature. Further, corrections are necessary for loss of heat, effects of dissocia-

tion, incomplete combustion, etc. For argon, Pier found that the specific heat does not vary with temperature.

31. Nernst's vacuum-calorimeter method is employed to find C_v at low temperatures. The gas is enclosed in the calorimeter [Fig. 9 (c)]. Eucken in this way found the specific heat of hydrogen between 35° and 273°K and obtained interesting results.

(c) METHODS BASED ON DETERMINATION OF γ

32. As already pointed out this is an indirect method of finding the specific heats of gases. Though indirect it is capable of the highest accuracy so that the modern accepted values of specific heats are based on the values of γ thus obtained.

The methods for measuring γ, the ratio of the two specific heats, may be classified under two heads: (1) those depending on the *adiabatic expansion or compression* of a gas, (2) those depending on the *velocity of sound* in the gas. We shall first consider the former.

(1) ADIABATIC EXPANSION METHOD

33. Experiments of Clement and Desormes.—Clément and Désormes were the first to find γ by the adiabatic expansion method. Their original apparatus has been considerably improved and is indicated in Fig. 14. A large flask A of about 28 litres capacity is closed by a stop-cock M about 1·4 cm. in diameter. The flask is connected to the manometer P_iP_A by means of a side-tube and is plugged with cotton wool to avoid loss of heat. First the flask is partially evacuated and the pressure p_i recorded by the manometer, is observed. The stop-cock M is then opened and quickly closed. Air rushes into the flask till the pressure inside and outside becomes equal. The process is adiabatic since the loss of heat in the short interval for which the stop-cock M is open may be neglected. The temperature of the air in the flask rises on account of the inrush of the external air and the pressure becomes atmospheric. The flask is next allowed to cool to the temperature of the surroundings when the water in the manometer rises and finally indicates the pressure p_f.

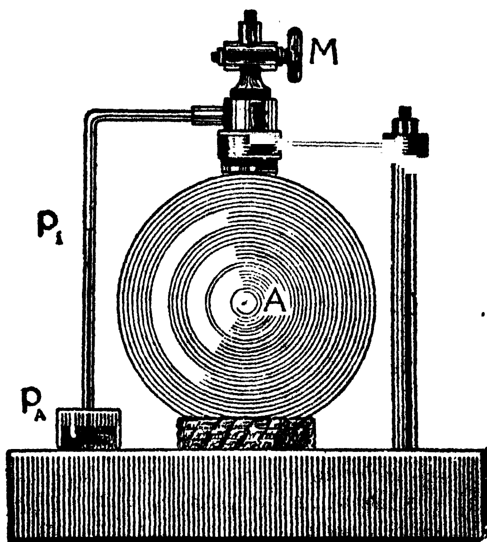


Fig. 14.—Clément and Désormes' apparatus.

Let the atmospheric pressure be p_A and the specific volumes of air at

the pressures, p_i, p_A, p_f, be respectively v_i, v_A, v_f. The first process is adiabatic and hence we have, assuming the gas to be perfect,

$$p_i v_i^\gamma = p_A v_A^\gamma . \qquad (30)$$

Since the final temperature is the same as the initial, we have, considering 1 gram of the gas,

$$p_i v_i = p_f v_f . \qquad (31)$$

Again,

$$v_A = v_f \qquad (32)$$

because the volume of the manometer tube is negligible compared with that of the flask and hence there will be no appreciable change in the specific volume of the gas due to rise of liquid in the manometer.

Combining (30), (31), and (32), we have,

$$\frac{p_i}{p_A} = \left(\frac{p_i}{p_f}\right)^\gamma,$$

or

$$\gamma = \frac{\log p_i - \log p_A}{\log p_i - \log p_f} .$$

If, as usual, the changes in pressure are small,

$$\gamma = \frac{p_i - p_A}{p_i - p_f} .$$

From the measurements of Clément and Désormes, Laplace deduced the value of γ to be 1·354.

In this experiment there is a source of serious error. We have assumed that the pressure inside has become atmospheric when the stop-cock M is closed. Actually, however, oscillations set in; on account of the kinetic energy more air first rushes in than would make the pressure just atmospheric, and hence the pressure inside becomes greater than p_A. Next some air rushes out till the pressure inside is less than p_A and so on. After several such overshootings the pressure p_A is attained. This takes considerable time and, as a matter of fact, this to-and-fro motion has not subsided when the stop-cock is closed. It must be closed at the instant when during an oscillation the pressure just becomes atmospheric. This is very difficult to secure and hence later investigators tried to avoid it by measuring the change in temperature resulting from adiabatic expansion. The stop-cock has not to be closed in this case. We shall consider shortly the experiments of Lummer and Pringsheim and of Partington and Shilling based on this principle.

We have assumed above that the incoming air has the same temperature as the air in the flask initially. To avoid correction in case it is not so, it is better to start with compressed gas in the flask, when a U-tube manometer must be used in place of $P_i P_A$. Further care must be taken to use perfectly dry air for γ is appreciably different for moist air. Consequently sulphuric acid is generally used as the liquid in the manometer.

34. Experiments of Joule, Lummer and Pringsheim, and Partington.— Joule was the first to study the change in temperature

by adiabatic expansion or compression. Various investigators later employed this method to determine γ. Air was compressed in a vessel and its temperature and pressure observed. It was then allowed to expand suddenly to atmospheric pressure and the change in temperature noted. The calculations can be easily made. If p_1, T_1 denote the pressure and temperature before expansion, p_2, T_2 the same quantities after the expansion, we have, from (25)

$$T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}}$$

or

$$(1-\gamma)\log\frac{p_1}{p_2} = \gamma \log\frac{T_2}{T_1},$$

$$\therefore\quad \gamma = \frac{\log p_1 - \log p_2}{(\log p_1 - \log p_2) - (\log T_1 - \log T_2)} \quad . \quad . \quad . \quad (33)^*$$

Thus γ can be calculated.

Lummer and Pringsheim made considerable improvements in the apparatus for determining γ by this method. They employed a 90-litre copper sphere and measured the change in temperature by the change in resistance of a thin bolometer wire hanging at the centre of this sphere. A Thomson galvanometer having a period of 4 sec. was used as a null instrument. Certain errors are, however, inherent in the apparatus.

In order to eliminate these errors Partington has further improved the apparatus. He used a large expansion vessel (130 litres capacity) and a bolometer of very thin platinum wire (·001 to ·002 mm. in dia-

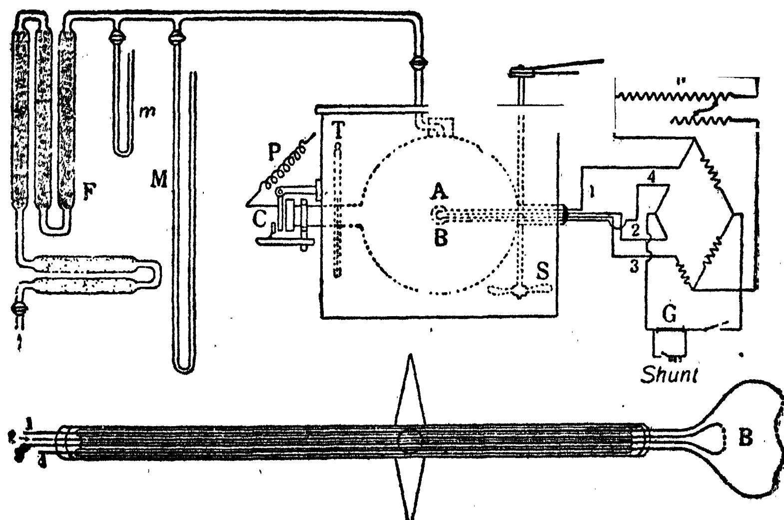


Fig. 15.—Partington's Apparatus.

meter) with compensating leads; thus there was no lag. Further an

* This is true for a perfect gas only. For real gases it requires modification.

Einthoven string galvanometer capable of recording temperature in ·01 sec. is used so that a detailed record of changes in temperature of the gas during and after expansion is obtained. His apparatus is indicated in Fig. 15. The vessel A is provided with the expansion valve C which can be manipulated by means of the spring P and whose size can also be varied. A is connected to the sulphuric acid manometer M, the mercury manometer m, and the drying tubes F. Thus carefully purified air enters A. Further the vessel A is kept immersed in a water-bath which is kept stirred by S. B is the bolometer wire (shown separately in the figure) and is connected in one arm of a Wheatstone bridge. G is the string galvanometer.

The initial temperature was read on a carefully standardised mercury thermometer T immersed in the bath and was given correct to ·01°. Then the resistance in one arm of the Wheatstone bridge was lowered to give some deflection in the galvanometer. It was so arranged by trials that immediately after expansion this deflection was reduced to zero. After the expansion experiment some ice was continuously added to the bath to keep its temperature constant and equal to that immediately after expansion. This was ascertained by keeping the galvanometer deflection steadily at zero, and the temperature of the bath was again read on the same mercury thermometer.

If the aperture is too large, oscillations of the gas take place and the galvanometer deflection is not quite steady, the initial deflection being somewhat greater than the true value. If the aperture is too narrow, prolonged expansion results and the process is not adiabatic. In practice, the aperture was gradually diminished and when overshooting was eliminated the deflection was instantaneous and perfectly steady. The atmospheric pressure was read on a Fortin's barometer and γ calculated from the foregoing formula. γ was found to be 1·4034* at 17°C. This method cannot be used at high temperatures since it is impossible to determine accurately the cooling correction.

35. Rüchardt's Experiment.— A simple method for determining γ, which is suitable for class-room demonstration, has been described by E. Rüchardt. The apparatus consists of a large glass bottle V (Fig. 16) fitted air-tight with a glass-tube at the top and a stop-cock H at the bottom. The glass-tube has a very uniform bore in which a steel ball of mass m fits very accurately. If the ball is dropped into the tube, it begins to oscillate up and down and comes to rest after a few oscillations. If the period of oscillation be determined with a stop-watch, γ can be easily calculated.

Let A be the cross-section of the glass tube, v the volume of the bottle, b the barometric pressure, and p the pressure in the flask. Then in the equilibrium position

$$p = b + \frac{mg}{A} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

* Using this, the velocity of sound in dry air at 0°C was calculated from equation (38) to be 331·38 metres which is in close agreement with Hebb's mean value 331·41 m./sec. (Sec. 37).

If the ball now moves a distance x downwards, it compresses the air adiabatically increasing the pressure to $p+dp$, hence its equation of motion is

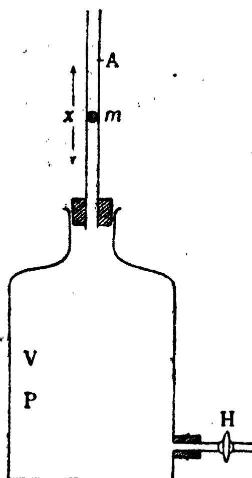
$$m\frac{d^2x}{dt^2} = \text{Force of restitution}$$
$$= -Adp.$$

Now since pv^γ = constant, we have

$$dp = -\gamma p\frac{dv}{v} = \gamma p\frac{Ax}{v}. \quad . \quad . \quad (35)$$

for $dv = -Ax$.

$$\therefore \quad m\frac{d^2x}{dt^2} = -\frac{\gamma pA^2x}{v}, \quad .. \quad . \quad (36)$$



from which the period of oscillation comes out to be

$$T = 2\pi\sqrt{\frac{mv}{\gamma pA^2}}$$

or

$$\gamma = \frac{4\pi^2mv}{pA^2T^2}. \quad . \quad . \quad . \quad (37)$$

Fig. 16.—Rüchardt's Apparatus.

Thus, knowing T, p and the constants of the apparatus, γ can be evaluated.

(2) Velocity of Sound Method

36. This method also depends upon the adiabatic expansion and compression of a gas but differs from the foregoing method in that no direct measurement of changes in temperature or pressure need be observed. The method has given us the most accurate data regarding specific heats for both high and low temperatures and so we shall consider it in some detail.

The velocity of sound in any fluid is given by the equation* $U = \sqrt{E_s/\rho}$ where E_s is the adiabatic elasticity of the fluid and ρ its density. For adiabatic changes in perfect gases† pv^γ = constant (p. 48), hence

$$E_s = -v\left(\frac{\partial p}{\partial v}\right)_s = \gamma p \text{ from } (35).$$

$$\therefore \quad U = \sqrt{\frac{\gamma p}{\rho}}. \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Thus, if we determine the velocity of sound in the gas we can find γ.

37. We may adopt either of the *two following methods*. The absolute velocity of sound in the gas may be determined, or we may

* See Barton, *Sound*.

† For real gases we must take into account the true equation of state (Chap. IV) and substitute the value of $(\partial p/\partial v)_s$ from that equation. In all accurate work this is done.

compare the velocity with that in another gas (say, air) which has been determined accurately by other methods.

For our purpose we discard the large-scale determinations of the velocity of sound in air on account of the various defects inherent in them. The most accurate direct determination of the velocity of sound in air was made by Hebb in 1905 by a method depending on the reflection of sound of known frequency from parabolic mirrors. His mean value after employing all corrections gives 331·41 metres/sec. as the velocity of sound in air at 0°C and 760 mm. pressure.

Now we must remember that practically all determinations of the velocity of sound in gases have been made in tubes, but the velocity in a tube is not the same as in free space. Corrections have to be applied to reduce this velocity to that in open space as explained in the next section. In equation (37) the velocity in open space must be substituted. Dixon has directly determined the velocity of sound in different gases from 15°C to 1000°C in a very satisfactory manner. His result may be employed to give γ.

Method based on the Measurement of Wavelength.

38. Kundt's Tube.—Kundt first devised an apparatus by means of which he could find the velocity of sound in a gas. This consists simply of a glass tube about 1 metre in length and 3 cm. in diameter. One end of the tube was fitted with a movable stopper, while through

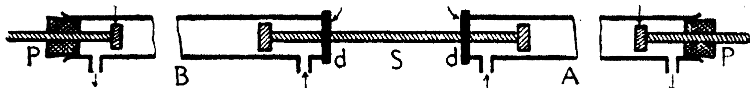


Fig. 17.—Kundt's Double-tube Apparatus.

the other end passed a loosely-fitting disc carried by a glass or metal sounding-rod which was itself clamped at its centre. Later Kundt employed the double-tube apparatus indicated in Fig. 17. Two tubes A and B are connected by means of the sounding-rod S which is clamped at distances one-quarter of its length from either end. The two rubber corks, d, d in the tubes A and B provide the clamping arrangement. The pistons P, P can be moved to and fro to bring the tubes in resonance with the rod S. Throughout the length of each tube is spread some light dust such as lycopodium powder or silica dust. One tube is filled with air and the other with the experimental gas. The sounding-rod S is excited by rubbing it at the centre when the dust is thrown into violent agitation at the antinodes and collects at the nodes. The distance between successive nodes equals half-wavelength, and knowing the frequency of the sound the velocity is easily obtained. The double form of the apparatus is very convenient for comparing the velocity of sound in any gas with that in air for

$$\frac{U_{\text{gas}}}{U_{\text{air}}} = \frac{\lambda_{\text{gas}}}{\lambda_{\text{air}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Various precautions are, however, necessary. The tube and the powder must be perfectly dry. Carefully purified air must be used or corrections* for the various impurities must be made. Too much dust should not be used for excess of dust diminishes the velocity. A decrease in the diameter of the tube diminishes the velocity. Finally, from the velocity in the tube the velocity in open space must be deduced. Though mathematical equations giving the requisite correction have been developed by Helmholtz, Kirchhoff and others, they are not quite adequate and the best method is to express the velocity U' in the tube as

$$U' = U(1-kC), \quad . \quad . \quad . \quad . \quad . \quad (40)$$

where U = velocity in open space,

k = a constant depending on the tube (its radius, thickness, thermal conductivity, surface, frequency of the sound, etc.)

C = a factor depending on the gas (its viscosity, density, ratio of specific heats, etc.)

Kirchhoff showed that

$$C = \sqrt{\frac{\eta}{\rho}} \left\{1+\sqrt{\epsilon}\left(\frac{\gamma-1}{\sqrt{\gamma}}\right)\right\}$$

where η = viscosity, ρ = density, γ = ratio of specific heats and $\epsilon = K/\eta c_v$, K being the thermal conductivity. For air from Hebb's experiments we know U, and by observing U' and calculating C, k for the tube is determined. This value of k is employed to give U the velocity in open space for any other gas.

Kundt and Warburg later employed this method to determine the velocity of sound in mercury vapour. One of the tubes contained mercury vapour and was heated in an air-bath to about 300°C. The distance between two nodes was measured when the tube cooled. They found $\gamma = 1{\cdot}666$. Ramsay employed this method to find γ for argon but on account of certain difficulties he got a low value. Behn and Geiger improved the apparatus considerably. They dispensed with the sounding rod and employed a sealed tube containing the experimental gas as the source of sound. This tube was clamped in its middle and was excited like the sounding-rod. The tube should be chosen properly and its length be adjustable so that the contained gas may give resonance with the sound emitted by the rod. The apparatus was eminently suited for gases at high temperatures. This method was later employed by different investigators particularly by Partington and Shilling.

* It can be easily shown from very simple considerations that for a mixture of perfect gases,

$$\frac{P}{\Gamma-1} = \frac{p_1}{\gamma_1-1} + \frac{p_2}{\gamma_2-1}$$

where p_1, p_2 are the partial pressures of these gases, P the total pressure and Γ stands for the ratio C_p/C_v for the mixture.

39. Experiments of Partington and Shilling.—These investigators determined the velocity of sound in various gases up to 1000°C by a resonance method. The apparatus is diagrammatically represented in Fig. 18.

FF is a silica tube 230 cm. long and wound over almost along its entire length with heating coils. To this tube is attached at X a glass tube, MM, 150 cm. long. Inside the former is the piston P of silica carried by the rod A, also of silica. BB is a steel tube joined to A by means of a cork. The tube BB carries a saddle I

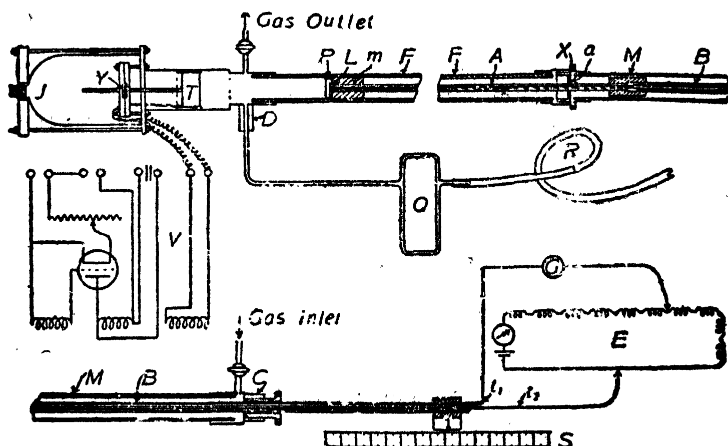


Fig. 18.—Partington and Shilling's Apparatus.

moving on a millimetre scale, thus the displacement of the piston can be found. Through this tube pass the thermo-couple leads to the potentiometer system E. The other end of the silica tube is closed by a telephone diaphragm T which can be moved by means of the screw Y. This end can be closed gas-tight by means of the bell-jar J. The telephone diaphragm is excited by a valve oscillator V giving a note of frequency 3000. D is a side-tube from which a rubber tube leads to the ear of the experimenter. X is an asbestos plug to prevent radiation of heat to M.

The silica tube is filled with the experimental gas and maintained at the desired temperature. The central tube AB is gradually moved away from D and the successive positions of the saddle I on the millimetre scale corresponding to a maximum sound in D are noted. The successive distances correspond to $\lambda/2$ and knowing the frequency the velocity is determined. The position of T has to be adjusted at different temperatures in order to give maximum sound in D when it will be at a distance $\lambda/2$ from the latter.

Cook employed this method to find γ for air and oxygen from 90° to 293°K. His apparatus may be visualized if we imagine the hot-air bath of Kundt and Warburg to be replaced by a long Dewar flask containing liquid air.

40. Specific heat of superheated or non-saturated vapour.—Regnault determined the specific heat of superheated or non-saturated steam and other vapours with an apparatus which was essentially similar to that shown in Fig. 12 (p. 49). Steam is superheated to $T°$ by passing it through the spiral S in the oil-bath kept at a temperature above 100°C. The superheated steam is next passed at constant pressure into the condenser kept immersed in the water calorimeter, and the rise in temperature of the latter from θ_1 to θ_2 noted.

If m is the mass of steam condensed, c_p its mean specific heat at constant pressure between the temperature T and its condensing point $\theta°$ at constant pressure, and L the latent heat of steam at $\theta°$, the quantity of heat given by the steam is

$$mc_p(T-\theta)+mL+m(\theta-\theta_2).$$

This must equal $w(\theta_2-\theta_1)$ where w is the thermal capacity of the calorimeter and its contents. Hence

$$mc_p(T-\theta)+mL+m(\theta-\theta_2)=w(\theta_2-\theta_1). \quad . \quad . \quad (41)$$

The experiment is then repeated with another value of T and a second equation similar to the above obtained. Solving the two equations, the two unknowns c_p and L are determined. Regnault thus found c_p for steam between 225°C and 125°C to be 0·48.

In case of vapours of other liquids, the specific heat of the liquid must be taken into account in writing out the above equations.

41. Results.—In the foregoing pages we have considered the various methods of finding specific heats. In table† 5 (p. 62) we give the values which best represent the experimental data. We reserve our comments on these values for the next chapter.

† Taken from *Handbuch der Experimentalphysik*, Vol. 8. p. 33.

Table 5.—Molar Heats in Calories at 20°C and Atmospheric Pressure.

Gas		C_p	C_v	$\gamma=\frac{C_p}{C_v}$	Remarks
Argon	...	4·97	2·98	1·666	Monatomic
Helium	...	4·97	2·98	1·666	
Hydrogen	...	6·865	4·88	1·408	Diatomic
Oxygen	...	7·03	5·035	1·396	
Nitrogen	...	6·95	4·955	1·402	
Nitric oxide	...	7·10	5·10	1·39	
Hydrochloric acid	...	7·04	5·00	1·41	
Carbon monoxide	...	6·97	4·98	1·40	
Chlorine	...	8·29	6·15	1·35	
Air	...	6·950	4·955	1·402	
Carbon dioxide	...	8·83	6·80	1·299	Triatomic
Sulphur dioxide	...	9·65	7·50	1.29	
Hydrogen sulphide	...	8·3	6·2	1·34	
Methane	...	8·50	6·50	1·31	Polyatomic
Ethane	...	12·355	10·30	1·20	
Acetylene	...	10·45	8·40	1·24	
Ethylene	...	10·25	8·20	1·125	
Ammonia	...	8·80	6·55	1·315	

42. Special Calorimeters.—Various types of calorimeters have been devised for special purposes *e.g.*, for the measurement of the heat of combustion, heat of chemical reaction, heat of dilution, etc., but they involve no new principles. Particular interest, however, attaches to the determination of heat of combustion in industries, for the value of fuel is judged mainly from its calorific value. This heat can be easily determined with the help of the calorimetric 'bomb'.

Fig. 19 indicates the calorimetric 'bomb'. It consists of a stout steel-cylinder A fitted with a cover held down tightly by suitable means. The cover has a milled-head screw valve which varies the cavity k_1 and thereby regulates the admission of oxygen through the tubes B and C into the bomb. Through the centre of the cover but insulated from it passes the wire i which is connected to the platinum wire w, the other end of the latter being connected to e. There is another similar screw valve varying the cavity k_2 through which gas can go out of the bomb. To enable the bomb to withstand the corrosive action of the products of combustion it is plated inside with gold, though platinum would be better. The bomb is enclosed in an

ordinary calorimeter such as is used for the method of mixtures. This calorimeter is provided with a stirrer and accurate mercury thermometer. The whole is surrounded by a constant temperature jacket.

To find the heat capacity of the bomb and its accessories a known amount of electrical energy may be spent in the system or a fuel of known calorific value burnt. The former method is adopted in standardising laboratories and the latter in actual practice. Benzoic acid is most suitable for this calibration. The fuel, if solid, is formed into a small briquette ; if liquid, it is soaked in pure cellulose and put in the platinum dish F and ignited. About three times the amount of oxygen just necessary for complete combustion is admitted through B, C. The oxygen is generally employed at a pressure of about 25 atmospheres and at this high pressure the combustion is almost instantaneous. As a result of these experiments it has been found that the calorific value of anthracite coal, wood (pine), petrol and methylated spirit are 8·8, 4·4, 11·3 and 6·4 kilocalories per gram respectively.

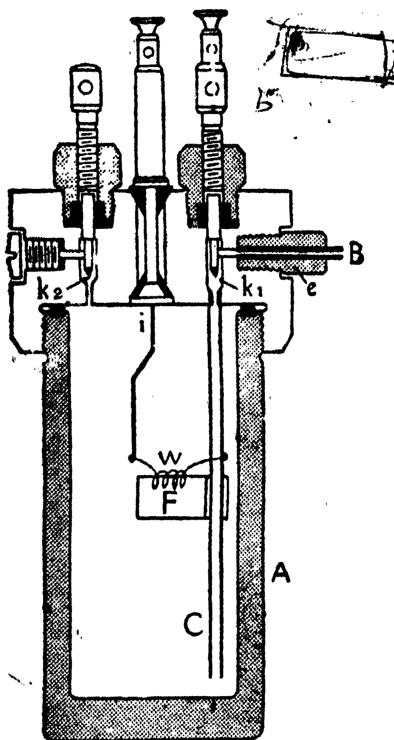


Fig. 19.—The Calorimetric Bomb.

43. Heat balance in the human body.—The temperature of the human body remains almost constant in health. The chief loss of heat is from the skin and from the excretory functions, the skin contracting in winter to diminish this loss. Heat is supplied to the body by the food we eat and by the oxidation of living tissues and muscles. The blood stream serves to keep the temperature of the body uniform. Due to the larger heat loss from the body in winter we have to take more food and cover ourselves with heavier clothes.

Books Recommended

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. I, article on 'Calorimetry'.

2. Partington and Shilling, *Specific Heats of Gases.*

3. *Handbuch der Experimentalphysik*, Vol. 8 Part I.

CHAPTER III

KINETIC THEORY OF MATTER

The Nature of Heat

1. Historical.—In the legends of some ancient nations, it is said that fire was first made for man by some friendly spirit by rubbing together two pieces of stick. The legend probably refers to a prehistoric discovery of the art of making fire. But though this way of producing heat by friction clearly indicates the real nature of heat, the early philosophers had no correct notion about it. They philosophized from the observation that heat could pass spontaneously from a hot body to a cold one. Heat was, therefore, supposed to be a kind of fluid—*the caloric fluid.*

Various fictitious properties were assigned to this hypothetical fluid. It was supposed to possess no weight, since bodies did not increase in weight on mere heating. Further, it was supposed to be highly elastic, all-pervading, indestructible and uncreatable by any process. The particles of this fluid were supposed to repel one another strongly which explained the expansion of bodies when heated and also the emission of heat during combustion. Temperature was likened to potential or level. When the body was heated the caloric fluid was supposed to stand at a higher level than when cold. Production of heat by friction was compared to the oozing out of water from a sponge when squeezed. The caloric fluid when thus squeezed out manifested itself as heat.

Doubts on the caloric theory of heat began to be thrown towards the end of the eighteenth century. The earliest philosopher to have a correct notion of the physical nature of heat was Count Rumford.* In those days guns were made by casting solid cylindrical pieces and scooping out the inside by a boring machine. Rumford in 1798 observed that apparently an inexhaustible amount of heat could be produced by the friction of the spindle of the boring machine against the body of the gun, though the amount of iron scraped was very small. He undertook protracted experiments and found that the amount of heat produced (measured by the raising of water to a high temperature) bore no relation to the amount of iron scraped, but was proportional to the amount of motion lost. He henceforth rejected the caloric theory and asserted that *Heat is only a kind of Motion. Whenever Motion disappears it reappears as Heat and there is an exact proportionality between the two. He even made an estimate* of what we now call the Mechanical Equivalent of Heat. His value is not much different from the value now adopted as standard.

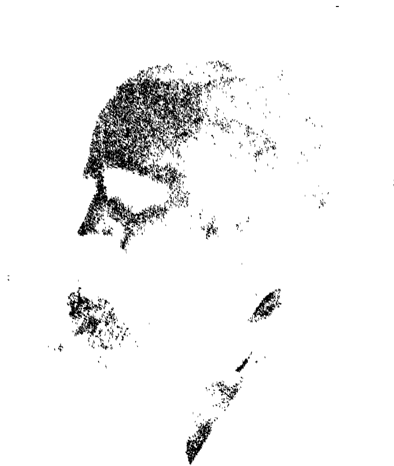
* Count Rumford (1753—1814) was born in North America. Being loyal to Great Britain during the American War of Independence, he had to flee from his country. He entered into the service of the Prince of Bavaria and later was placed in charge of the arsenal at Munich when he performed the celebrated experiments on the boring of guns. In 1799 he went to London and was one of the founders of the Royal Institution.

To face p. 64.



JAMES PRESCOTT JOULE (1818—1880) (p. 65)

Born near Manchester, Joule was educated at home. The main work which occupied the greater part of his life was on the relationship between work and heat. He established the principle of the mechanical equivalent of heat.



James Clerk Maxwell (1831—1879) (p.75)

Born in Edinburgh, educated at Edinburgh and Cambridge. He became Professor of Physics at Marischal College, Aberdeen, in 1856, at King's College, London, in 1860 and Professor of Experimental Physics in charge of Cavendish Laboratory, Cambridge, in 1871. His greatest work was in connection with the development of the kinetic theory of gases and the foundation of the electromagnetic theory of light.

In 1799, Davy showed that when two pieces of ice were rubbed together water is produced. It was admitted by all that water has greater quantity of heat than ice.† Now supporters of the caloric theory asserted that heat is generated in friction because the substance produced by friction has less capacity for heat than the original substance. But the substance produced in Davy's experiment (water) has greater heat capacity than ice, hence the caloric theory became untenable. Davy's experiment proved the greatest stumbling block for the caloric theory.

But the valuable work of Rumford and Davy was soon forgotten and it was only about forty years later that the first law of Thermodynamics gained general publicity through the researches of Joule in England, Mayer and Helmholtz in Germany, and Colding in Denmark.

2. Joule's Experiments.—In 1840 J. Joule of Manchester began his classical experiments for determining the relation between the work done and heat generated. We do not wish to describe these experiments here in detail as they are at present only of historical interest. The heat was produced by churning water contained in a cylinder by means of brass paddles. This could be kept revolving by means of a double thread wound over a solid cylinder and passing over pulleys, and carrying weights at either end. The amount of work done was calculated by observing the height through which the weights fell. The rise in temperature was measured by a mercury thermometer and hence the heat generated could be found. After applying various corrections Joule found that 772 ft.-lbs. of work at Manchester can raise the temperature of 1 pound of water 1°F. In 1878 Joule used a modified form of the apparatus in which the work done was measured by the application of an external couple as in Rowland's experiments to be described later (§ 5.)

3. First Law of Thermodynamics.—The conversion of work into heat was thus established by the experiments of Rumford and Joule. Now, between the times of Rumford and Joule, the steam-engine had been widely applied for various industrial purposes. As we shall see later, this is simply a contrivance for the conversion of heat into work. Thus it is established that heat and work are mutually convertible. Nay, we may go even further and say that when some work is spent in generating heat, a definite relation exists between the work spent and heat generated. These two facts, *viz.*, the possibility of converting work into heat and *vice versa* and the existence of a definite relation between the two are expressed by the First Law of Thermodynamics. Mathematically, the law may be stated thus:—

If W is the work done in generating an amount of heat H, we have,

$$W = JH, \qquad (1)$$

† This was proved by Black's discovery of Latent Heat of Fusion. He hung equal masses of ice and ice-cold water alternately inside a room and observed that the water was raised 4°C in half-an-hour, while the ice took about ten hours to melt into water, the temperature remaining constant.

where J is a constant, provided all the work done is spent in producing heat and no portion is wasted by friction, radiation, etc. If H is expressed in calories and W in ergs, $J = 4{\cdot}186 \times 10^7$. The truth of the second statement embodied in the law is amply proved by the fact that the various methods for finding J (secs. 4—7) yield almost identical values.

4. Methods for determining J.—Various methods have been devised for finding the value of the mechanical equivalent of heat but the method of fluid friction and the electrical method are the only ones capable of yielding accurate results, and hence only these will be considered in detail. There is, however, an ingenious method of calculating the value of J which was first given by J. R. Mayer in 1842. From the theoretical relation $J(C_p - C_v) = R$ (p. 46), he calculated the value of J. Thus, for hydrogen $R = p_0 V_0 / T_0 = 8{\cdot}314 \times 10^7$ ergs per mol per °C (pp. 6, 10) and $C_p - C_v = 1{\cdot}985$ cal. per mol per °C (p. 62).

$$\therefore \quad J = \frac{8{\cdot}314 \times 10^7}{1{\cdot}985} = 4{\cdot}18 \times 10^7 \text{ ergs per calorie.}$$

Certain other methods* that have been employed are enumerated below:—

(1) Measurement of heat produced by compressing a gas—Joule.

(2) Heat produced by percussion—Hirn.

(3) Work done by a steam-engine.

This was used by Hirn in 1862. He measured the amount of steam entering the cylinder of the steam-engine in a given time at a known temperature and pressure. The total heat rejected by the engine was found by conducting the waste steam into a calorimeter, and the heat loss due to cooling and other causes was estimated. Thus the net amount of heat which is converted into work is obtained. The work done by the engine was found from an indicator diagram (Chap. IX.). Equating these two Hirn got a value of $J = 4{\cdot}18 \times 10^7$ ergs per calorie.

(4) Heat developed in a cylinder kept stationary in a rotating magnetic field produced by means of polyphase alternating electric current—Baille and Ferry.

5. Rowland's Experiments.—Joule's thermometers were not standardised and thus errors of 1 or 2% may arise from this cause. The rate of rise of temperature in his experiment was rather slow (about 0·62°C per hour) and hence the radiation correction was large. Rowland minimised this source of uncertainty by designing a special apparatus with the object of securing a rapid rate of rise of temperature (40°C per hour), the principle of the method being identical with that of Joule.

* For a complete list of the methods see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p. 480.

The calorimeter was firmly attached to a vertical shaft *ab* [Fig. 1 (*a*)] to which is fixed a wheel *kl* wound round with a string carrying weights, *o*, *p* at either end, the whole being suspended by a torsion

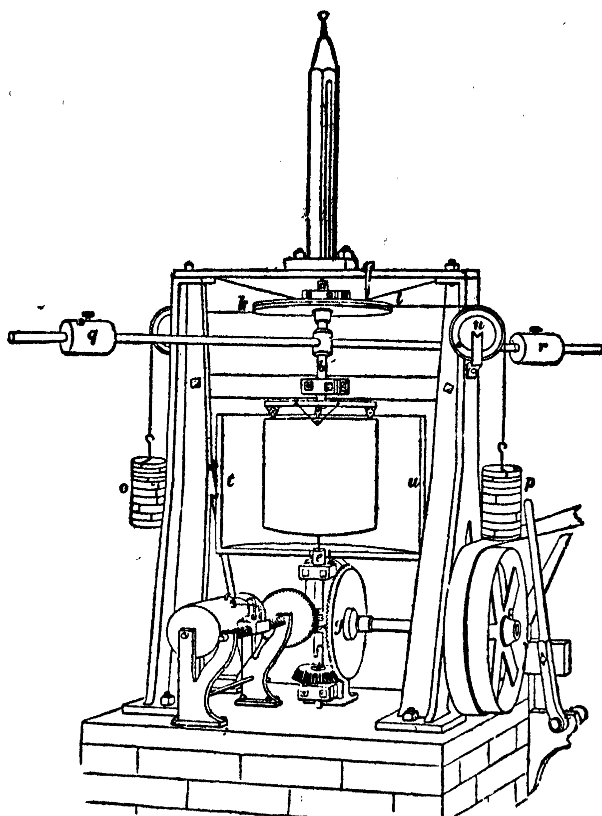


Fig. 1 (*a*).—Rowland's Apparatus.

wire. The axis of the paddle [Fig. 1 (*b*)] passed through the bottom of the calorimeter and was attached to the shaft *ef*. The latter could be rotated uniformly by the wheel *g* driven by a steam-engine. The number of revolutions was automatically recorded on a chronograph worked by a screw on the shaft *ef*. The revolution of the paddle at an enormous rate tended to rotate the calorimeter in the same direction on account of fluid friction. This was prevented by the external couple produced by the weights *o*, *p* and the torsion wire. For the purpose of accurately determining the radiation correction a water jacket *tu* surrounded the calorimeter.

The paddle is indicated separately in Fig. 1 (*c*). To a hollow cylindrical axis four rings were attached, each having eight vanes.

Around these were the fixed vanes, consisting of five rows of ten each, which were fixed to the calorimeter. Thus the liquid could

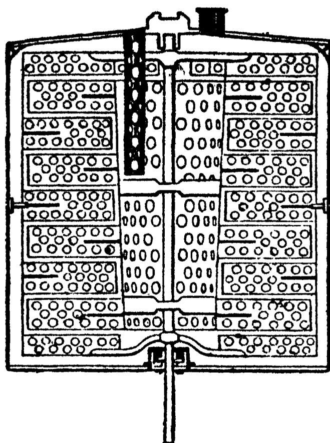


Fig. 1 (*b*).

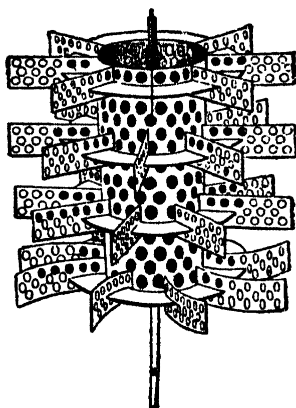


Fig. 1 (*c*).

be vigorously churned. The rise of temperature was recorded by a thermometer suspended within the central sieve-like cylinder in which water circulated briskly.

If D denotes the diameter of the torsion wheel and mg, mg, the weights suspended, the work W done in n revolutions of the paddle is given by

$$W = \text{couple} \times \text{angle of twist} = mgD.\ 2\pi n. \quad . \quad . \quad . \quad (2)$$

If M denotes the thermal capacity of the calorimeter and its contents, $\delta\theta$ the rise in temperature (corrected for radiation), the heat produced by friction is $M\delta\theta$, hence

$$J = \frac{2n\pi . mgD}{M\delta\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If D is in cm. and mg in dynes, J comes out in ergs per calorie.

Corrections were applied for the torsional couple, for the weights in air which must be reduced to vacuum, for the expansion of the torsion wheel, etc. Rowland found $J = 4{\cdot}179 \times 10^7$ ergs for the 20° calorie. Laby recalculated from Rowland's observations by applying corrections and obtained the value $J = 4{\cdot}187 \times 10^7$ ergs for the 15° calorie.

Reynolds and Moorby obtained by a modified apparatus, the value of the mean calorie between 0° and 100°C to be $4{\cdot}1833 \times 10^7$ ergs. Hercus and Laby employed what is in principle an induction motor, to find J, and obtained the value $J = 4{\cdot}186 \times 10^7$ ergs per calorie.

6. A Simple Laboratory Method of finding J.—For laboratory purposes a simple apparatus for finding J due to G. F. C. Searle is shown in Fig. 2, but the accuracy attained by this apparatus is not great. A is a brass cone held rigidly in position by means of

non-conducting ebonite pieces attached to a brass cylinder C, which can be made to revolve by means of a motor. Inside A is another brass cone B fitting smoothly into it and attached rigidly to a wooden disc D. The latter has a groove running round its circumference and carrying a cord which passes over the pulley P and supports a weight *mg*. When the outer cone rotates rapidly the inner one tends to move in the same direction on account of the friction between the two cones, but is held in position by properly suspending a suitable weight *mg* at the end of the cord. The inner cone B contains some water, a thermometer and a stirrer (not shown).

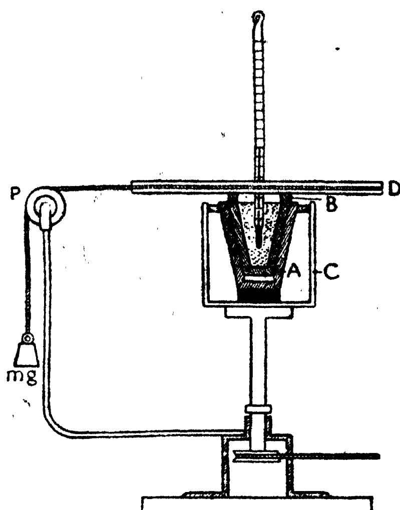


Fig. 2.—A simple laboratory apparatus for *J*.

When the weight *mg* is kept stationary the turning moment exerted by it just balances the frictional couple. If *D* is the diameter of the disc the frictional couple is $mgD/2$ and the work done by it in n revolutions of the cone is $2n\pi.mgD/2$. If M be the water equivalent of the cones and the contents, $\delta\theta$ the rise of temperature produced by friction, then

$$n\pi mgD = Jm\delta\theta, \qquad . \quad . \quad . \quad . \quad (4)$$

whence J can be calculated.

7. Electrical Methods.—These methods have already been described (pp. 37-41) in full detail. It is easily seen that if the specific heat of the liquid be known, this method gives the mechanical equivalent of heat. There are two methods:—(1) Steady-flow method, (2) Rise in temperature method. The former was employed by Callendar and Barnes who did their experiments with great care and skill, but the principal source of uncertainty in their work lies in the value of the electrical units employed. According to Laby we may put the E.M.F. of the Clark cell used by Callendar and Barnes as 1·4335 volts at 15°C. They employed the international ohm which is equal to $1{\cdot}0005 \times 10^9$ e.m. units. Reducing Callendar's results with the help of these data Laby gets for the mechanical equivalent of the 20° calorie a value of $4{\cdot}1795 \times 10^7$ ergs. This yields $4{\cdot}1845 \times 10^7$ ergs as the equivalent of the 15° calorie. The most accurate experiments on the subject are those of Jaeger and Steinwehr by the rise of temperature method, and of Laby and Hercus by the mechanical method, the respective values being $4{\cdot}1863 \times 10^7$ and $4{\cdot}1860 \times 10^7$ for the 15° calorie. Osborne, Stimson and Ginnings have recently found

the value 4·1858 by the electrical method. Hence, we can adopt the value $4 \cdot 186 \times 10^7$ ergs per calorie.

Exercise.—Joule found that 778 ft.-lbs. of work can raise the temperature of 1 pound of water 1°F. Calculate the mechanical equivalent of heat in C.G.S. units.

$$778 \text{ ft. lbs.} = 778 \times 30 \cdot 48 \times 453 \cdot 6 \text{ gm.} \times \text{cm.}$$
$$= 778 \times 30 \cdot 48 \times 453 \cdot 6 \times 981 = 1 \cdot 055 \times 10^{10} \text{ ergs.}$$

Heat produced $= 453 \cdot 6 \times \frac{5}{9} = 252$ calories.

$\therefore \quad J = 1 \cdot 055 \times 10^{10} / 252 = 4 \cdot 187 \times 10^7$ ergs per calorie.

8. Heat as Motion of Molecules.—From these experiments it is clearly established that heat is a kind of motion; the next question is —*motion of what?* The answer was given by Clausius and Krönig in 1857 for the case of gases. They said that heat consists in the motion of molecules or the smallest particles of matter.

The idea that if we go on dividing matter we ultimately come to small particles which cannot be further sub-divided dates from very ancient times. But it remained a barren speculation till Dalton gave to it a definite form in the middle of the last century. The history of the molecular theory is known to all our readers and no account of it need be given here. Suffice it to say that according to it all matter is composed of a large number of molecules, all molecules of the same substance being exactly identical* as regards mass, size, etc. but differ in their motion. In the solid and liquid states these molecules are closely packed while in gases they are far apart from one another.

Now according to the Kinetic Theory of Matter heat is supposed to consist in the motion of these molecules. The identification of heat with motion of molecules is not a mere hypothesis. It is able to explain and predict natural phenomena and at present there is little doubt that it rests upon solid foundations of truth.

9. Growth of the Kinetic Theory.—The Kinetic Theory of matter rests upon two fundamental hypotheses: (1) the molecular structure of matter, (2) the identification of heat with molecular motion. The first of these was established early in the 19th century while the second was established by the experiments of Rumford, Joule, Mayer and Colding. We may, however, consider Daniel Bernouilli (1730) as the founder of the modern kinetic theory as he was the first to explain Boyle's law by molecular motions. Clausius and Maxwell in the middle of the 19th century placed the theory on a firm mathematical basis. Among the other prominent contributors to the theory are Boltzmann, Meyer, Jeans, van der Waals, Lorentz and Lord Rayleigh.

Up to the beginning of the present century, however, the theory, had been developed entirely from a mathematical stand-point. There was no direct experimental proof of the actual existence of these molecules or of their motions. Gradually, however, much evidence has

* Since the discovery of isotopes this remark requires some modification.

The formula also shows that the molecules of the lightest gas, *viz.*, hydrogen, would move faster than the molecules of any other gas under the same conditions.

13. Deduction of Gas Laws.—From the above results we proceed to deduce the laws of perfect gases.

(1) *Avogadro's* Law.*—If there are two gases at the same pressure p we have from (9)

$$p = \tfrac{1}{3}m_1n_1C_1^{\,2} = \tfrac{1}{3}m_2n_2C_2^{\,2}, \qquad (12)$$

where the subscripts 1 and 2 refer to the first and the second gas respectively. Further, if the two gases are also at the same temperature we know there will be no transfer of heat (or energy, since the two are equivalent by the First Law of Thermodynamics) from one to the other when they are mixed up. On mixing, the two types of molecules will collide against one another and there will be a mutual sharing of energy. Maxwell† showed purely from dynamical considerations that the condition for no resultant transfer of energy from one type of molecules to the other is that the mean translational energy of molecules of the one type is equal to that of the other. Hence if the two gases are at the same temperature it follows that

$$\tfrac{1}{2}m_1C_1^{\,2} = \tfrac{1}{2}m_2C_2^{\,2}. \qquad (13)$$

Combining (12) and (13) we get

$$n_1 = n_2. \qquad (14)$$

i.e., two gases at the same temperature and pressure contain the same number of molecules per c.c. This is Avogadro's Law.

(2) *Boyle's Law.*—Equation (10) states that the pressure of a gas is directly proportional to its density or inversely proportional to its volume. This is Boyle's Law. This holds provided C^2 remains constant which, as shown above, implies that the temperature remains constant.

(3) *Dalton's Law.*—If a number of gases of densities ρ_1, ρ_2, ρ_3, ... and having mean square velocities $C_1^{\,2}$, $C_2^{\,2}$, $C_3^{\,2}$....., be mixed in the same volume, the resultant pressure p, considering each set of molecules, is given by

$$p = \tfrac{1}{3}\rho_1C_1^{\,2}+\tfrac{1}{3}\rho_2C_2^{\,2}+\tfrac{1}{3}\rho_3C_3^{\,2}+\ldots\ldots\ldots$$
$$= p_1+p_2+p_3+\ldots \qquad (15)$$

* Count Amedeo Avogadro di Quaregna (1775—1856) was born in Turin where he was Professor of Physics from 1833 to 1850. His chief work is Avogadro's law.

† Maxwell considered the collision of gaseous particles of two different types and possessing different amounts of energy. By applying the dynamical laws of impact viz. conservation of momentum and energy, he found that after each collision the difference in energy of the two molecules diminishes by a certain fraction, i.e. the molecule possessing greater energy loses it while that possessing less energy gains. This process is repeated at each collision, and ultimately the energies of the two become equal. For details, see the Authors' *Treatise on Heat* (1958), pp. 845-847.

i.e., the pressure exerted by the mixture is equal to the sum of the pressures exerted separately by its several components. This is Dalton's law of partial pressures.

§ 14. Introduction of Temperature.—If we consider a gram-molecule of the gas which occupies a volume V, equation (10) yields

$$pV = \tfrac{1}{3} MC^2, \qquad (16)$$

M being the molecular weight. In order to introduce temperature in the foregoing kinetic considerations of a perfect gas we have to make use of the experimental law, *viz.*, $pV = RT$. Hence

$$RT = \tfrac{1}{3}MC^2,$$

or

$$C^2 = \frac{3RT}{M} \qquad (17)$$

Thus C^2 is proportional to the absolute temperature which may thus be considered proportional to the mean kinetic energy of translation of the molecules. This is the kinetic interpretation of temperature. Hence, according to the kinetic theory, the absolute zero of temperature is the temperature at which the molecules are devoid of all motion. This deduction is, however, not quite justified since the perfect gas state does not hold down to the absolute zero. The interpretation given by thermodynamics is somewhat different (Chap. X) and is more reasonable. That does not necessarily require that all motion should cease at the absolute zero.

We can put $M = Nm$ where m is the mass of a single molecule and N the number of molecules in a gram-molecule, which is usually called the *Avogadro* number.

We can put $R/N = k$ where k is a constant. k is known as Boltzmann's constant. Hence we get

$$p = (N/V)kT = nkT,$$

where n denotes the number of molecules per c.c. Further from (17)

$$\tfrac{1}{2}Nm\overline{c^2} = \tfrac{3}{2}NkT,$$

or

$$\tfrac{1}{2}m\overline{c^2} = \tfrac{3}{2}kT, \qquad (17a)$$

i.e., the mean kinetic energy of translation of one molecule is $\tfrac{3}{2}kT$.

Exercise.—Calculate the molecular kinetic energy of 1 gram of helium at N.T.P. What will be the energy at 100°C?

From (17) the kinetic energy is equal to

$$\tfrac{1}{2}\overline{c^2} = \tfrac{3}{2}\frac{RT}{M} = \tfrac{3}{2}\frac{8{\cdot}3 \times 10^7 \times 273}{4} = 8{\cdot}5 \times 10^9 \text{ ergs.}$$

Energy at 100°C $= 8{\cdot}5 \times 10^9 \times 373/273 = 1{\cdot}16 \times 10^{10}$ ergs.

§ 15. Distribution of Velocities. Maxwell's Law.—In the above we were concerned only with the mean square velocity and did not care to find the velocity of every molecule. But for studying the properties of the gas further we must know the dynamical state of the whole system. It is easy to see that all the molecules cannot have the same speed for even if at any instant all the molecules

possess the same speed, collisions at the next moment will augment the velocity of some and diminish that of the others. As the number of molecules is very large ($2\cdot7 \times 10^{19}$ per c.c. at N.T.P.) and they are too small to be visible even in the ultra microscope, we do not interest ourselves in the behaviour of individual molecules. We treat the problem statistically and apply the theory of probability. We shall illustrate this by means of an example. In a big city there are persons of all ages and we find the number of persons whose ages lie between definite ranges, say between 10 and 15, 15 and 20, and so on. So in an assemblage of molecules where the molecules have all velocities lying between 0 and infinity we find the number of molecules dn_c possessing velocities lying between c and $c+dc$. In the steady state this number remains constant and is not modified by collisions. This number is given by the distribution law of Maxwell which states:

$$dn_c = 4\pi n a^3 e^{-bc^2} c^2 dc, \quad . \quad . \quad . \quad (18)$$

where n is the number of molecules per c.c. and $a = \sqrt{b/\pi} = \sqrt{m/2\pi kT}$. But we cannot say what the velocity of any individual molecule selected at random is. We can only say that the probability that its velocity lies between c and $c+dc$ is

$$4\pi a^3 \, e^{-bc^2} c^2 dc.$$

Thus the distribution law gives a complete knowledge of the gas only in a statistical sense.

A slight transformation (putting $bc^2 = x^2$) will show that the number $dn = 4n\pi^{-\frac{1}{2}} x^2 e^{-x^2} dx$, which helps us to represent the law graphically. Let us plot the function $y = 4\pi^{-\frac{1}{2}} e^{-x^2} x^2$ against x

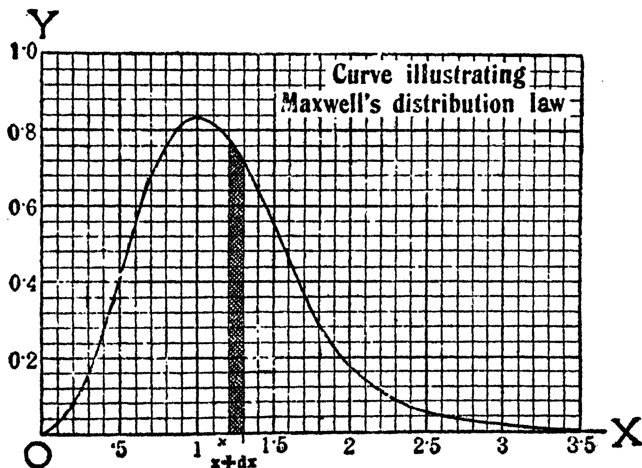


Fig. 5.—Curve illustrating Maxwell's Law.

(Fig. 5). Then the number dn of molecules whose speed lies between

x and $x+dx$ is proportional to the shaded area. The ordinate y gives the fraction of the number of molecules possessing a speed corresponding to x, and from the curve it is obvious that the probability corresponding to $x=1$ is greatest, while it is considerably less for $x=2$ or $x=\frac{1}{2}$. Hence we can approximately treat the whole gas as endowed with the most probable velocity corresponding to $x=1$.

16. Average Velocities.—We must distinguish between two velocities, the square root C of the mean square velocity, and the mean velocity $\bar{c}$. The former is such that its square is the average of the squares of the velocities of the molecules. Thus

$$C^2 = \overline{c^2} = \frac{1}{n}\int_0^\infty c^2 dn_c = \frac{3}{2b} = \frac{3kT}{m} \quad . \quad . \quad . \quad . \quad (19)$$

which we have already obtained in (17).

The mean velocity

$$\bar{c} = \frac{1}{n}\int_0^\infty c\, dn_c = \sqrt{\frac{8kT}{m\pi}} \quad . \quad . \quad . \quad . \quad (20)$$

$$\therefore \quad \frac{\bar{c}}{C} = \sqrt{\frac{8}{3\pi}} = \cdot 921 \quad . \quad . \quad . \quad . \quad (21)$$

The most probable velocity α is that value of c for which N_c the number of molecules with velocity c is maximum. Hence for such value of c, $\frac{dN_c}{dc} = 0$. This relation gives α. Substituting for N_c we get

$$\alpha = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2}{3}}\, C. \quad . \quad . \quad . \quad . \quad (22)$$

An interesting consequence of the large molecular velocities is seen in the almost complete absence of an atmosphere from the surface of the moon. Dynamical investigations show that if a particle is projected from the Earth with a velocity exceeding $\sqrt{2gr_0}$ where g is the gravity at the surface of the earth and r_0 its radius, it will never return to the earth and will be lost in space. This critical velocity is about 11 kilometres per second for Earth and 2·4 kilometres for the moon. Russian scientists have quite recently (2nd January, 1959) been able to launch a cosmic rocket "Mechta" which overcame the Earth's gravitational barrier and flew past the moon into space to become the first artificial planet of the sun with an orbital period of 447 days.

Calculations show that the average velocity of hydrogen at ordinary temperatures is about 1·8 kilometres per second and according to Maxwell's law a large number of molecules have velocities much greater and also much less than this. Thus all molecules having velocity greater than the critical will escape from the planet. Due to molecular collisions a certain fraction will always have velocity greater than the critical and will escape. This *loss of the planetary atmosphere* will continue indefinitely. It is for this reason that there

is practically no atmosphere on the surface of the moon while the atmosphere of the Mars is much rarer than that of the earth.

17. Law of Equipartition of Kinetic Energy.— We next proceed to deal with the law of equipartition of energy. It is better to introduce here the idea of *degrees of freedom* of a system. Suppose we watch an ant constrained to move along a straight line; it has then only one degree of freedom and its energy is given by $\frac{1}{2}m\dot{x}^2$. If it is allowed to move in a plane the energy is given by $\frac{1}{2}m\dot{x}^2+\frac{1}{2}m\dot{y}^2$. An ant cannot have more than two degrees of freedom, but a bee which is capable of flying has three degrees of freedom, all of translation. Thus a material particle, supposed to be a point, can have at most three degrees of freedom. A rigid body can, however, not only move but also rotate about any axis passing through itself. The most general kind of rotatory motion can be resolved analytically into rotations of the body about any three mutually perpendicular axes through a point fixed in itself. Hence the degrees of freedom contributed by rotational motion are three. We may now state the definition of the term 'degrees of freedom'. The total number of independent quantities which must be known before the position and configuration of any dynamical system can be fully known is called the number of *degrees of freedom* of the system.

Now it can be shown from rigorous dynamical considerations that the energy corresponding to every degree of freedom is the same as for any other, *i.e.*, *the energy is equally distributed between the various degrees of freedom.* This is the law of equipartition of kinetic energy and was arrived at by Maxwell* in 1859. Boltzmann† extended it to the energy of rotation and vibration also. It can further be shown that the energy corresponding to each degree of freedom per molecule is $\frac{1}{2}kT$‡. This law is very general, but we shall not attempt here to prove it.

Thus if any dynamical system has n degrees of freedom, the energy associated with it at T°K is $n\times\frac{1}{2}kT$.

18. Molecular and Atomic Energy.—The above theorem is very useful in calculating molecular energy of substances. Let us calculate the specific heat of gases. In a *monatomic* gas the molecules are identical with atoms and if, as a first approximation, we assume the atom to be a structureless point, then from the previous considerations each molecule has got three degrees of freedom and will have the kinetic energy equal to $3\times\frac{1}{2}kT$. In the state of a perfect gas the

* Maxwell, *Collected Works*, Vol. I, p. 378.

† Ludwig Boltzmann (1844-1906). Born and educated in Vienna, he was Professor of Theoretical Physics at Vienna, Graz, Munich and Leipzig. On account of his fundamental researches he is regarded as one of the founders of the kinetic theory of gases.

‡ Equation (17*a*) gives $\frac{1}{2}m\overline{c^2}=\frac{3}{2}kT$, i.e., the mean kinetic energy of translation per molecule is $\frac{3}{2}kT$. If we assume that the energy is equally distributed between the three degrees of freedom, the energy associated with one degree of freedom per molecule becomes $\frac{1}{2}kT$. For a formal proof of the law see the Authors' *Treatise on Heat*, §3·26.

molecules possess only kinetic energy and no potential energy. The total energy E associated with a gram-molecule is N times the above expression. It is thus equal to $\frac{3}{2}NkT = \frac{3}{2}RT$. The molar specific heat at constant volume is therefore

$$C_v = \frac{dE}{dT} = \tfrac{3}{2}R = 2{\cdot}98 \text{ cal./degree.}$$

For all perfect gases we have established the relation

$$C_p - C_v = R.$$

Therefore, for a monatomic gas

$$C_p = \frac{3R}{2} + R = \frac{5}{2}R = 4{\cdot}96 \text{ cal./degree.}$$

and the ratio of the two specific heats

$$\gamma = 5/3 = 1{\cdot}66. \quad . \quad . \quad . \quad . \quad (23)$$

These theoretical conclusions agree with experimental results (see Table 5, Chap. II) for the monatomic gases like argon, helium, etc.

The specific heat of polyatomic gases can also be obtained by using the equipartition law. The molecule of a *diatomic* gas may be pictured as a system of two atoms (assumed to be points) joined rigidly to one another like a dumb-bell. This system possesses, in addition to the three components of the velocity of translation of the common centre of gravity, two components of the velocity of rotation about two axes perpendicular to the line of centres of the two atoms. Thus the system has five degrees of freedom and the total energy $E = \frac{5}{2}RT$. Hence

$$C_v = \tfrac{5}{2}R, \quad C_p = \tfrac{7}{2}R, \quad \gamma = 1{\cdot}4. \quad . \quad . \quad . \quad (24)$$

This is approximately the case for hydrogen, nitrogen, etc. (p. 62). At low temperatures, however, C_v falls to $\frac{3}{2}R$, as Eucken's experiments with hydrogen show, indicating that the rotation has disappeared. For chlorine C_v is greater than $\frac{5}{2}R$. This shows that the two atoms are not rigidly fixed but can vibrate in a restricted manner along the line of centres.

In a *triatomic* gas a molecule possesses three translational and three rotational degrees of freedom and hence

$$C_v = 6 \times \tfrac{1}{2}R = 3R, \quad C_p = 4R, \quad \gamma = 1{\cdot}33. \quad . \quad . \quad (25)$$

For more complex molecules γ approaches unity but is always greater than it. It is not possible to calculate in a simple way the energy of internal vibration of such molecules since the vibrations are not freely and fully developed.

An expression for the specific heat of solids may also be obtained from the kinetic theory. We can consider molecules of a solid as elastic spheres held in position by the attraction of other molecules and capable of vibrating in a simple harmonic manner about a mean position. The molecule will have three components of velocity, and hence three degrees of freedom. The kinetic energy associated with each degree of freedom is $\frac{1}{2}kT$. On the average the harmonic vibration

will have equal kinetic and potential energies and hence the total energy associated with each degree of freedom is kT. Therefore, the total energy for N molecules for the three degrees of freedom is $3RT$, and the molar specific heat is $3R = 5{\cdot}955$. This yields Dulong and Petit's law.

But the kinetic theory of specific heat is unable to explain the variation of specific heat with temperature (p. 45), particularly, the marked decrease at extremely low temperatures. Further, the decrease is gradual and cannot be explained by the disappearance of any degree of freedom which would involve discontinuous changes by multiples of $\frac{1}{2}R$. We cannot assume fractional degrees of freedom. Here the principles of classical dynamics and equipartition law fail completely. The quantum theory of specific heat has been developed which explains the existing facts satisfactorily.

MEAN FREE PATH PHENOMENA

19. Need for the Assumption that Molecules have got a finite Diameter.— We have seen in the previous sections that the molecules of a gas are moving at ordinary temperatures with very large velocities; in the case of air it amounts to about 400 metres per sec. There is no force to restrain the motion of the molecules. Hence the objection was raised that the assumption of such large rectilinear velocities was incompatible with many facts of observation. If the particles are moving with such enormous velocities, the gaseous mass contained in a vessel would disappear in no time. But we are all aware that the top of a cloud of smoke holds together for hours, hence there must be some factor which prevents the free escape of particles.

A very simple explanation was offered by Clausius. He showed that the difficulty disappears if we ascribe to the molecules a finite though very small volume. Then as a particle moves forward, it is sure to collide with another particle after a short interval, and its velocity and direction of motion will be completely changed. The path traversed between two successive collisions will be a straight line described with a constant velocity, since the molecules exert no force over one another except during collision. Hence the path of a single particle will consist of a series of short zig-zag paths as illustrated in Fig. 6.

Some of these paths will be long, others will be short. We can define a mean free path λ. Add up the lengths of a large number of paths and divide it by the total number; this will give λ. This quantity is of great importance in studying a class of phenomena, called transport phenmena, such as viscosity, conduction of heat and diffusion.



Fig. 6.—Illustration of free path

20. Calculation of the Mean Free Path.— We shall give a very simple method of calculating the mean free path approximately. We

make the simplifying assumption that all molecules except the one under consideration are at rest. The moving molecule will collide with all those molecules whose centres lie within a distance σ from its centre (σ being the diameter of the molecules), and are thus contained in a sphere of radius σ described about the centre of the moving molecule. As the molecule traverses the gas with velocity v it will collide with all the molecules lying in the region traversed by its sphere of influence. The space thus traversed in a second is a cylinder of base $\pi\sigma^2$ and height v, and hence of volume $\pi\sigma^2 v$. If the number of molecules per c.c. is n, this cylinder will enclose $\pi\sigma^2 vn$ centres of molecules and hence the number ν of collisions per second is $\pi\sigma^2 vn$. The length of the mean free path

$$\lambda = \frac{v}{\nu} = \frac{v}{\pi\sigma^2 vn} = \frac{1}{n\pi\sigma^2}. \quad . \quad . \quad . \quad (26)$$

In the above we assumed the other molecules to be at rest. Maxwell corrected this expression by introducing into the foregoing considerations the motion of all molecules according to Maxwell's distribution law and obtained the result

$$\lambda = \frac{1}{\sqrt{2}\, n\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The average number of collisions suffered by a molecule per second is $\bar{c}/\lambda$.

21. Transport Phenomena.—The distribution law expressed by (18) may also be put in the form

$$dn = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m(u^2+v^2+w^2)}{2kT}} du\, dv\, dw, \quad . \quad . \quad (28)$$

where dn is the number of molecules with velocity components lying between u and $u+du$, v and $v+dv$, w and $w+dw$ respectively. If the gas is endowed with mass motion represented by u_0, v_0, w_0, then

$$dn = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(U^2+V^2+W^2)} dU\, dV\, dW, \quad . \quad (29)$$

where $U = u - u_0$, $V = v - v_0$ and $W = w - w_0$.

If the gas is not in a steady state any one of the following cases, singly or jointly, may occur. (1) Firstly u_0, v_0, w_0 may not have the same value in all parts of the gas so that there will be a relative motion of the layers of the gas with respect to one another. We have then the phenomenon of viscosity. (2) Secondly, T may not be the same throughout, then we have the phenomenon of conduction, *viz.*, heat will pass from regions of higher T to regions of lower T. (3) Thirdly, if n is not the same everywhere we have the case of diffusion, *i.e.*, molecules diffuse from regions of higher concentration to regions of lower concentration. It is thus obvious that viscosity, conduction and diffusion represent respectively the transport of momentum, energy and mass. These are called transport pheno-

mena. These phenomena are brought about by the thermal agitation of the molecules. But the molecules move with very large velocities, while these processes are comparatively very slow. The cause of this anomaly lies in the frequent molecular collisions. Hence the study of these phenomena is most conveniently done through the mechanism of mean free path. The molecules carry with them certain associated magnitudes and thereby tend to establish equilibrium.

22. Viscosity. We shall first discuss the phenomenon of viscosity. Here we shall give an elementary treatment of the phenomenon based on considerations of mean free path. Consider a gas in motion and choose a horizontal plane xy such that there is a mass motion of the gas parallel to xy-plane but no mass motion along the z-axis. Assume that the mass-velocity u_0 increases upwards as z increases. The molecules above the plane $z = z_0$ possess, on the average, greater momentum than those below it, and hence when molecules from either side cross the plane there is greater transport of momentum downwards, since the number of molecules moving each way is the same, there being no mass motion parallel to the z-axis.

We can consider every molecule, on the average, to traverse a distance λ equal to the mean free path and then suffer a collision. If the velocity gradient is du_0/dz the difference in the mean molecular velocity across two planes separated by a distance* λ is $\lambda\, du_0/dz$. The mass of a molecule being m, the difference in momentum is $m\lambda du_0/dz$. Again, due to heat motion, the number of molecules moving along the x-axis must be, on the average, the same as that moving along the y- or the z-axis. Hence one-third of the molecules may be considered as moving along the z-axis, both up or down, or only one-sixth may be considered as moving in the upward direction. Consider unit area of the observation plane z_0. The number of molecules crossing this area per second in the upward direction will be† $\frac{1}{6}n\bar{c}$ where n is the molecular density and $\bar{c}$ the mean molecular velocity corresponding to the temperature of the gas, since all those molecules contained in a cylinder of base unity and height $\bar{c}$ cross the unit area in one second. Hence the momentum transferred across the plane in the upward direction is $\frac{1}{6}n\bar{c}\left(G - m\lambda\frac{du_0}{dz}\right)$ where G is the momentum corresponding to the observation plane. Similarly, for molecules going downwards the momentum transferred is $\frac{1}{6}n\bar{c}\left(G + m\lambda\frac{du_0}{dz}\right)$. Hence the total momentum transferred downwards is $\frac{1}{3}n\bar{c}.m\lambda\frac{du_0}{dz}$. This will exert an accelerating force on the lower layers. Or the lower layers

* Actually we must take the average resolved part of λ along the z-axis. This comes out to be $\frac{2}{3}\lambda$ instead of λ.

† Rigorous calculation shows that this will be $\frac{1}{4}n\bar{c}$.

will retard this faster layer by a force equal to this. By definition of viscosity η this force must equal $\eta du_0/dz$. Hence

$$\eta = \tfrac{1}{3}mn\bar{c}\lambda = \tfrac{1}{3}\rho\bar{c}\lambda, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where ρ is the density of the gas.

23. Discussion of the Result.—We have established that $\eta = \frac{1}{3}\rho\bar{c}\lambda$ but $\lambda = \dfrac{1}{\sqrt{2}\ n\pi\sigma^2}$ (p. 82), hence

$$\eta = \frac{1}{3\sqrt{2}}\frac{m\bar{c}}{\pi\sigma^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Now $\bar{c}$ is proportional to the square root of the absolute temperature, hence the coefficient of viscosity is independent of the pressure or the density of the gas, provided the temperature is constant. This deduction is rather surprising and was first regarded with suspicion. Mayer and Maxwell subsequently showed experimentally that the law actually held for pressures lying between 760 mm. and 10 mm., and this was a striking success for the Kinetic Theory. But beyond both limits the law fails. At higher pressures deviation from the law is expected since the intermolecular forces cannot be then ignored. At low pressures the mean free path λ gradually increases till it becomes comparable with the dimensions of the containing vessel, and then remains constant. Any further decrease of pressure reduces ρ and hence η. Thus at very low pressures the coefficient of viscosity rapidly decreases with decrease of pressure.

Again since $\bar{c}$ varies as $1/\sqrt{m}$, η for different gases should vary as $\sqrt{m}$. This is found to be approximately true.

24. Conduction.—Let us now find an expression for the conductivity of a gas which is a similar problem. In this case the temperature and hence the energy varies from layer to layer and it is the energy E which is transferred from one layer to another. Considering the energy gradient $\dfrac{d\bar{E}}{dz}$ instead of the momentum gradient $m\dfrac{du_0}{dz}$, the total transfer of energy downwards per unit area becomes

$$\tfrac{1}{3}n\bar{c}\lambda\frac{d\bar{E}}{dz},$$

where $\bar{E}$ denotes the mean molecular energy pertaining to any layer.

If K be the conductivity of the gas, $\dfrac{dT}{dz}$ the temperature gradient, the flow of energy across unit area in the downward direction is $JK\dfrac{dT}{dz}$, where J is the mechanical equivalent of heat. Therefore

$$JK\frac{dT}{dz} = \tfrac{1}{3}n\bar{c}\lambda\frac{d\bar{E}}{dT}\frac{dT}{dz},$$

or

$$K = \tfrac{1}{3}n\bar{c}\lambda\frac{d\bar{E}}{dT}\frac{1}{J} = \tfrac{1}{3}n\bar{c}\lambda mc_v = \eta c_v \quad . \quad . \quad . \quad . \quad (32)$$

when c_v is expressed in heat units. Further considerations show that the above result must be modified into $K = \epsilon\eta c_v$ where ϵ is some constant.

Since $K = \epsilon\eta c_v$ and the variation of c_v is small, the variation of conductivity with pressure and temperature follows in general the same course as the variation of viscosity. Thus conductivity like viscosity is independent of pressure. This was verified experimentally by Stefan and others. We shall not consider the phenomenon of diffusion as it is somewhat more complicated.

25. Value of Constants.—The value of the root mean square velocity for a gas was calculated numerically for nitrogen on p. 75. The mean velocity $\bar{c}$ can be calculated from (21) and is equal to $\cdot 92 \times 4\cdot 93 \times 10^4 = 4\cdot 5 \times 10^4$ cm./sec. Then (30) gives, on substituting $\eta = 166 \times 10^{-6}$ gm. cm^{-1} sec^{-1},

$$\lambda = \frac{3\eta}{\rho\bar{c}} = \frac{3 \times 166 \times 10^{-6}}{1\cdot 25 \times 10^{-3} \times 4\cdot 5 \times 10^4} = 9 \times 10^{-6} \text{ cm.}$$

The number of collisions suffered by a molecule per second is

$$\frac{\bar{c}}{\lambda} = \frac{4\cdot 5 \times 10^4}{9 \times 10^{-6}} = 5 \times 10^9.$$

Assuming $n = 2\cdot 7 \times 10^{19}$ per c.c. we have

$$\sigma = \left(\frac{1}{\sqrt{2}n\pi\lambda}\right)^{\frac{1}{2}} = \left(\frac{1}{\sqrt{2} \times 2\cdot 7 \times 10^{19} \times 3\cdot 14 \times 9 \times 10^{-6}}\right)^{\frac{1}{2}} = 3 \times 10^{-8} \text{ cm.}$$

These values will give an idea of the numerical magnitudes involved in the kinetic theory of gases. We give below several constants for most gases at 0°C and atmospheric pressure.

Table 1*

Gas	Mass of molecule $m \times 10^{24}$ gm.	Velocity in metres per sec.	Viscosity $\eta \times 10^6$ in gm. cm.$^{-1}$ sec.$^{-1}$	Thermal conductivity $K \times 10^6$ in cal. cm.$^{-1}$ sec.$^{-1}$ °C^{-1}	Mean free path $\lambda \times 10^6$ cm.	Molecular diameter $\sigma \times 10^8$ cm.
H_2	3·1	1839	86	318	18·3	2·47
N_2	43·1	493	166	52	9·44	3·5
O_2	49·2	461	187	56	9·95	3·39
He	6·1	1311	189	339	28·5	2·18
A	61·3	413	210	38·9	10·0	3·36
Cl_2	58·5	307	129	..	4·57	4·96

* The table is largely taken from Kaye and Laby, *Tables of Physical and Chemical Constants*, Longmans Green & Co., 1948. No great accuracy is claimed for the values given.

Book Recommended.

A good account of the subject-matter of this chapter will be found in Eugéne Bloch, *Kinetic Theory of Gases*, English translation published by Methuen and Co.

Other References

1. Jeans, *Kinetic Theory of Gases* (1940), Camb. U. P.
2. Kennard, *Kinetic Theory of Gases* (1938), McGraw-Hill.

CHAPTER IV

EQUATIONS OF STATE FOR GASES

1. Deviation from the Perfect Gas Equation.—By the term "Equation of State" is meant the mathematical formula which expresses the relation between pressure, volume and temperature of a substance in any state of aggregation. If any two of these quantities be known, the third has a fixed value depending uniquely upon them, and can be determined if the equation of state is known, but this is seldom possible. According to the laws of Boyle and Charles, we have for a perfect gas,

$$pV = RT. \qquad (1)$$

This is the equation for a perfect gas.

But even Boyle himself found that the law held only under ideal conditions, *viz.*, high temperature and low pressure, while under ordinary conditions it did not correctly represent the true state of affairs for any actual gas. For every temperature a curve can be drawn which has for its abscissa the volume and for its ordinate the corresponding pressure of the enclosed substance. These curves are called isothermals. If equation (1) were true the isothermals ought to be rectangular hyperbolas parallel to each other, but experiments show that this is very seldom the case. The most extended earlier investigations are due to Regnault. He applied pressures up to 30 atmospheres while the temperature was varied from 0° to 100°C. He plotted the product pV as ordinate against p as abscissa (see Figs. 6, 7 *infra* this chapter). The curves ought to be straight lines parallel to the x-axis ; actually, however, they were inclined to it. He found that for air, nitrogen and carbon dioxide the product pV decreases with increasing pressure, while for hydrogen it increases. He also found that hydrogen shows an abnormal Joule-Thomson effect (Chap. VI). These facts led him to describe hydrogen as "more than perfect". If equation (1) were true the product pV ought to remain constant ; thus these permanent gases were shown to be imperfect.

Later work by Natterer, Andrews and Cailletet using higher pressures confirmed the idea that the actual gases showed considerable deviations from equation (1). Andrews' experiments are of fundamental importance as they throw much light on the actual behaviour of gases and form the basis of an important equation of state first proposed by van der Waals. Andrews' experiments are described in the next section.

The most thoroughgoing and exact experiments are due to Amagat who investigated the behaviour of various gases up to a pressure of 3,000 atmospheres. His results particularly with CO_2 (Fig. 7) and ethylene showed that their behaviour is very complicated.

A different method has been utilized by K. Onnes who, investigated the behaviour of several gases at very low temperatures and found that none of the numerous equations of state proposed correctly represents the results of experiments. He finds that at any tempera-

ture the results are best represented by an empirical equation of the type

$$pV = A + Bp + Cp^2 + Dp^3 + \dots, \qquad (2)$$

where A, B, $C \dots$, are constants for a fixed temperature, but vary with temperature in a complicated manner. As many as twenty-five constants are used ; they are called *virial coefficients*. A is simply equal to RT while the values of the coefficients of higher terms diminish rapidly. Holborn and Otto, following Onnes' method, studied several gases up to 100 atmospheres and between the temperatures of $-183°C$ and $+400°C$, and found that they need take only four constants. They give the values of these constants for various gases at different temperatures.

The coefficient B is of particular importance. For all gases it varies in a similar way: at low temperatures it has a negative value, then it gradually increases to zero and becomes positive. Now if at any temperature $B = 0$, and C, D are negligible as usual, then

$$\frac{d(pV)}{dp} = B = 0.$$

Hence, at this temperature Boyle's law will be obeyed up to fairly high pressures. This temperature is called the *Boyle Point* T_B.

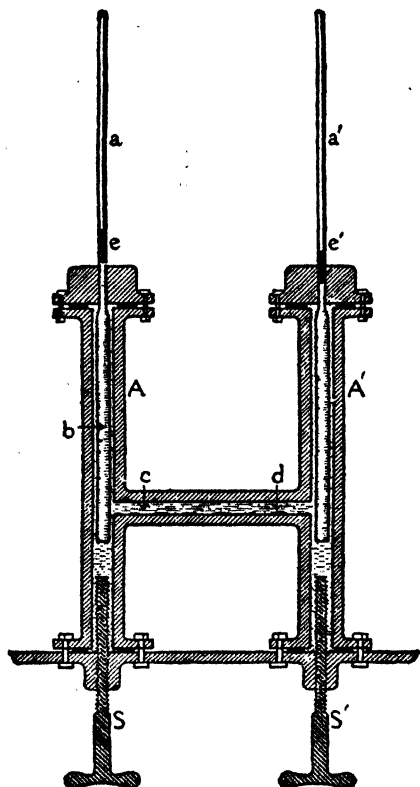


Fig. 1.—Andrews' apparatus.

2. Andrews' Experiments.—While engaged in the attempt to liquefy some of the so-called permanent gases—an important problem of those days, Andrews,* in 1869, was led to study the isothermals of carbon dioxide. His apparatus is indicated in Fig. 1. *ab* is a glass tube whose upper portion consists of capillary tube and is narrower than the lower part. Carefully dried carbon dioxide was passed through the tube for several hours and then the tube sealed at both ends. The lower end of the tube was immersed under mercury and opened, and some of the gas expelled by heat, so that, on cooling, a small column of mercury rose in the tube and enclosed the experimental gas.

* Thomas Andrews (1813-1855). Born in Belfast, he was Professor of Chemistry at Queen's College, Belfast, from 1845 to 1879. He is remembered chiefly for his work in connection with the liquefaction of gases.

The tube was surrounded by a strong copper tube A fitted with brass flanges at either end, to which brass pieces could be attached airtight with the help of rubber washers. A screw S passed through the lower flange. The tube A contained water and by screwing in pressures as high as 400 atmospheres could be applied to the carbon dioxide enclosed above *e*. To register the pressure a similar capillary tube containing air was placed on the right side, and was enclosed in a tube A′, exactly similar to A, with which it communicated through the tube *cd* and thus the pressures in both the tubes were always kept equal. The pressure in either tube could be varied by means of the screws S or S′. The capillary tube *ac* could be surrounded by any suitable constant temperature bath (not shown).

3. Discussion of Results.—The curves obtained by Andrews are shown in Fig. 2. Let us consider the isothermal corresponding to 13·1°C. Starting from the right we see (portion AB) that as we increase the pressure, the volume diminishes considerably and finally liquefaction of the gas begins at a pressure of about 49 atmospheres (point B). As long as liquefaction continues the pressure remains constant and the volume continually diminishes, more and more of the gas being precipitated as liquid. This is indicated by the nearly horizontal line BC. (The slight inclination indicating an increase of pressure towards the end is due to the presence of air as impurity). At C all the gas has condensed into liquid and the almost vertical rise of the curve indicated by CD corresponds to the fact that liquids are only slightly compressible.

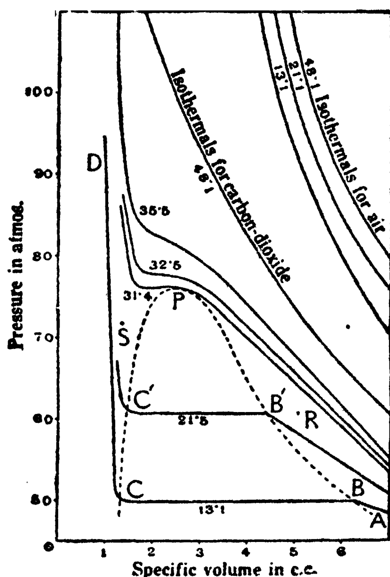


Fig. 2.—Isothermals for Carbon dioxide.

The isothermal corresponding to 21·5°C is of the same general form but the horizontal portion B′C′ is shorter. In this case the specific volume of the vapour when condensation begins is smaller while that of the liquid when condensation has completed is greater than the corresponding volumes for the previous curve. As the temperature is raised these changes proceed in the same direction as above, till at 31·4°C the horizontal part has just disappeared and the two volumes have become identical. This is called the *critical isothermal* for carbon dioxide. Above this temperature, the horizontal part is absent from all the isothermals and as we increase the pressure,

there is no visible formation of liquid, but the volume diminishes rapidly till it becomes nearly equal to the volume of the liquid at a slightly lower temperature. This peculiarity of the isothermal also disappears at higher temperatures as is evident from the isothermal for 48·1°C which is much like the isothermals for air shown separately on the right-hand top.

We thus see that the whole diagram for carbon dioxide is divided by the critical isothermal into two essentially different regions. Above this isothermal no liquid state is at all possible even under the greatest pressure, while below it there are three separate regions. In the region enclosed by the dotted curve BB′PC′C whose highest point P, called the *critical point* lies on the critical isothermal, both liquid and gaseous states coexist. To the left of the line PC and below the critical isothermal there is the liquid region while to the right of PB there is the gaseous region. Now if, by means of gradual changes, we want to convert gaseous CO_2 at 25°C and 60 atm. pressure (represented by the point R) into liquid CO_2 at the same temperature (represented by the point S) without any discontinuity appearing, *i.e.*, the mass is not to separate into a liquid and a gaseous part with a layer between them, we must avoid reaching the inside of the dotted curve BB′PC′C. Thus we heat the substance above 31·4° and then compress it till the volume becomes equal to that of the liquid at that temperature. Next cool it to 25°C and then reduce the pressure. Thus starting from the point R which undoubtedly represents a gaseous state we are able to reach, by means of gradual changes, the point S which undoubtedly represents liquid state, while at no stage of the operation any heterogeneity or meniscus appears in the whole mass. This result is expressed by the statement that *there exists a continuity of the liquid and gaseous states* and was established by the experiments of Andrews.

We have seen that if gaseous carbon dioxide is compressed above 31·4°C no liquid can make its appearance, however great the pressure may be. More accurate experiments show that this temperature is 31·0° and not 31·4°. The temperature 31·0°C is called the *critical temperature* (T_c) for carbon dioxide. We may define critical temperature as the highest temperature at which a gas can be liquefied by pressure alone. This is why the earlier attempts to liquefy the permanent gases failed, though enormous pressures amounting to as much as 3,000 atmospheres were sometimes employed. The pressure necessary to liquefy gases at the critical temperature is called the critical pressure (p_c) and the volume which the gas* then occupies, *i.e.*, at the critical temperature and critical pressure, is called the *critical volume* (V_c). These three quantities are called the *critical constants* of a gas. A table giving the critical constants for various gases is given on p. 102. It obviously follows that in trying to liquefy a gas, it is useless to apply pressure alone if the initial temperature is above the critical point and no pressure greater than the critical need be employed.

* Of course the volumes occupied by the gas and the liquid at the critical temperature are the same.

4. **Van der Waals' Equation of State.** The equation of state for perfect gases was deduced theoretically from the kinetic theory of gases (Chap. III). There we assumed that the molecules have no volume and do not exert forces of attraction on one another. These assumptions are correct only for the ideal or perfect gas to which the actual gases of nature approximate at low pressure and high temperature. Rigorously speaking, however, all gas molecules have finite size whose importance was first pointed out by Clausius. For our present purpose we shall treat the molecules as hard elastic spheres. It is clear that at very high pressures the total volume of all the molecules will not be a negligible fraction of the volume of the gas and further even at the highest possible pressure the volume occupied by the substance cannot be less than the volume occupied by the molecules when they are most closely packed. It follows, therefore, that the free volume of the gas to which the Boyle-Charles' law refers is not the gas volume V but is less than V by a factor b where b is related to the total volume of the gas molecules.

Another simple way of arriving at this result is from considerations of collisions. Consider four balls lying separated from one another on a line perpendicular to the wall and let the farthest one start to move towards the wall with a fixed velocity. If the balls are big, the distance to be traversed is less and hence the last ball will strike the wall earlier than when the balls are mere points. Similarly for molecules of finite size the number of collisions with the walls and hence the pressure will be greater than for point molecules. Thus the effect of molecular size is equivalent to a reduction in the total volume of the gas by b.

Hirn, in 1864, pointed out that the molecules must exert forces of attraction on one another, hence the energy cannot be wholly kinetic, and potential energy due to forces of cohesion must also be taken into account. The correction for forces of cohesion can be very simply obtained. These forces are of the same nature as those which give rise to the phenomenon of surface tension in liquids. The molecules attract one another with a force which varies inversely as some power of the distance between them. Thus the force will be appreciable only for small distances and is negligible for larger ones. A molecule in the interior is acted on by forces in all directions and hence these will balance; but this is not so with a molecule on the surface or close to it. The components of the forces acting on it resolved parallel to the surface will balance but not those in a perpendicular direction. There will be a resultant force acting perpendicular to the boundary layer and directed inwards. It is obvious that this force on a single molecule will be proportional to the number of attracting particles in the fluid, *i.e.*, to the number n of molecules per c.c. The force acting per unit area of the gaseous boundary will be proportional to the product of the above force and the number of molecules in that area. Hence the cohesive force p_1 acting per unit area of the boundary layer of the gas is proportional to n^2. Now $n = N/V$ where N is the total number of molecules and V the total volume. Therefore $p_1 \propto 1/V^2$. This force opposes the outward motion of the molecules

and thus decreases their momentum and hence also the pressure generated by their impact. Hence the pressure will be less than that calculated previously by the factor a/V^2, where a is some constant. In other words, we must replace p in the perfect gas equation by $p + \frac{a}{V^2}$ as if the external pressure p on the gas is increased by a/V^2.

Applying both these corrections the gas equation becomes

$$\left(p + \frac{a}{V^2}\right)\left(V - b\right) = RT. \quad . \quad . \quad . \quad . \quad (4)$$

This is van der Waals' equation*. Detailed considerations show that b is equal to *four* times the total volume of the molecules. Van der Waals† was the first to work out a systematic theory, taking into account both these factors, viz., the finite size of molecules and the forces of cohesion. Van der Waals' equation is found to hold true for small deviations from the perfect gas equation. A comparison of this with the experimental results is given in sec. 6. Various other equations of state have been proposed. Some of them are more accurate than van der Waals' equation in certain regions; nevertheless, the latter, considering its simplicity, gives in general, the most satisfactory first approximation to the behaviour of actual gases. We shall discuss this equation in more detail.

5. Method of finding the Values of 'a' and 'b'—A method of finding the values of 'a' and 'b' occurring in van der Waals' equation is given below:—

Determination of 'a' and 'b' from Critical Data.—In the next section it will be shown from theoretical considerations that the critical temperature T_c, critical pressure p_c and critical volume V_c, for a gas obeying van der Waals' equation are respectively given by

$$T_c = \frac{8a}{27bR} \;;\quad p_c = \frac{a}{27b^2} \;;\quad V_c = 3b. \quad . \quad . \quad . \quad (5)$$

$$\therefore \quad a = \frac{27R^2}{64} \cdot \frac{T_c^2}{p_c}; \quad b = \frac{R}{8} \cdot \frac{T_c}{p_c}. \quad . \quad . \quad . \quad . \quad (6)$$

Thus if T_c, p_c are experimentally determined 'a' and 'b' can be calculated with the help of equation (6). It may, however, be pointed out that the method is not very accurate as the gas does not obey van der Waals' law accurately near the critical point. But this is not of much consequence as 'a' and 'b' themselves depend upon temperature and volume. The values of 'a' and 'b' for a few important gases are given in table 1. They refer to 1 c.c.‡ of gas at N.T.P., and are determined by this method from equation (6).

* For the various methods of deducing this equation see the Authors' *Treatise on Heat* (1958), Chap. X.

† Johannes Diderik van der Waals (1837-1923) was born at Leyden. In 1873 he formulated his equation of state and established the continuity of liquid and gaseous states. In 1877 he became Professor at Amsterdam and was awarded the Nobel Prize in 1910.

‡ If we consider a gram-molecule we have to multiply 'a' in the table by $(22{\cdot}4\times10^3)^2$ and 'b' by $(22{\cdot}4\times10^3)$. This is obvious from relation (6) since R for a gram-molecule in these units (atm.$\times$cm.^{3}) is $22{\cdot}4\times10^3/273$.

Tables 1.—Values of 'a' and 'b' for some gases.*

Substance	$a \times 10^5$ in atm. $\times$ cm^4.	$b \times 10^5$ in c.c.
Helium	6·8	106
Argon	268	143
Oxygen	273	143
Nitrogen	272	173
Hydrogen	48·7	118
Carbon dioxide ..	717	191
Ammonia	833	166

Exercise.—Using the values of $T_c = 5{\cdot}3$, $p_c = 2{\cdot}25$ atm., calculate 'a' and 'b' for helium for a gram-molecule.

$$a = \frac{27R^2}{64} \frac{T_c^2}{p_c} = \frac{27 \times (8{\cdot}3 \times 10^7)^2 \times (5{\cdot}3)^2}{64 \times 2{\cdot}25 \times 1{\cdot}01 \times 10^6} \text{ dynes} \times \text{cm.}^4 = 3{\cdot}5 \times 10^4$$
atm. $\times$ cm.^{4}

$$b = \frac{R}{8} \frac{T_c}{p_c} = \frac{5{\cdot}3 \times 8{\cdot}3 \times 10^7}{2{\cdot}25 \times 8 \times 1{\cdot}01 \times 10^6} = 24 \text{ c.c.}$$

6. Discussion of van der Waals' equation.—We shall now discuss van der Waals' equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT.$$

This is an equation of the third degree in V, hence it follows that for every value of p, V must have three values. Further, from theory of equations, either all the three values are real or one is real and two imaginary.

Again writing the equation in the form

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad . \quad . \quad (7)$$

we see that for very large values of V, p is small and in the limit $p = 0$ when $V = \infty$. Again, when V is very small approaching b, p tends to infinity. Hence the curve must have a concavity upwards. Further V cannot be less than

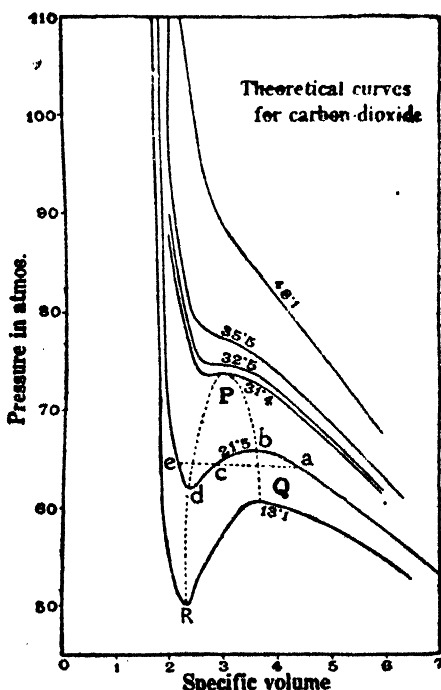


Fig. 3—Theoretical curves for CO_2 according to van der Waals' Equation.

* Taken from Landolt and Bornstein, *Physikalische-Chemische Tabellen.*

b for then p would be negative which is physically absurd. If in (7) we substitute the values of 'a' and 'b' for carbon dioxide *viz.*, $a = 0{\cdot}00717$ atm. × cm.[4], $b = 0{\cdot}00191$ c.c. and then represent the resulting equation by means of graphs for every temperature (p=ordinate, V=abscissa), curves of the type shown in Fig. 3 are obtained. It is readily seen that the curves resemble, in general, the experimental curves (Fig. 2) obtained by Andrews, but if we look for quantitative agreement by trying to make the two sets of curves coincide we are greatly disappointed. In fact, the agreement is only approximate and qualitative partly because of errors in the assumed values of 'a' and 'b' and partly, because the equation holds only approximately.

There is, however, a remarkable divergence between the theoretical and the experimental curves in one region. The theoretical curves drawn from van der Waals' equation give maxima and minima in the region represented by straight lines in Andrews' curves. Experimentally, this is the region where condensation or vaporisation begins and the pressure remains constant as long as the process continues.

This difference is easily explained when the theoretical curve is properly interpreted. The part bd inside the dotted curve corresponds to the fact that the volume should decrease with decrease of pressure which is quite contrary to experience. This would be a collapsible state, for any decrease of volume is accompanied by a decrease of pressure which tends to further decrease the volume. (This is apparent if we imagine the fluid to be confined in a cylinder.) Thus the state of the fluid inside the dotted curve represents a state of unstable equilibrium, and consequently, can never be realised in practice. This is why the part bcd is not obtained in Andrews' experiments. The portion ab represents supersaturated vapour and is sometimes obtained experimentally as, for example, when air containing water vapour is compressed beyond the point when condensation would usually occur, without condensation occurring. This happens when the air is free from dust or charged ions which act as nuclei for condensation. This state is, however, unstable and is easily disturbed by the introduction of particles of dust, etc. Hence the portion ab which represents supersaturated vapour in unstable equilibrium does not occur in Andrews' curves which represent only states of stable equilibrium. Similarly, the portion de represents a superheated liquid which is also in unstable equilibrium and is obtained experimentally when gas-free liquid is carefully heated. Hence this also does not occur in Andrew's curves. Thus the apparent divergence is explained.

Van der Waals' theory, however, does not tell us when condensation begins, *i.e.*, where the straight part commences. A simple thermodynamic argument* shows that the straight portion should be so drawn that the area $abca$ = area $cdec$.

* Let the substance represented by the point a form the working substance of a heat engine (Chap. IX) and let it be taken through the cyclic operation represented by the path $abcdeca$. Since the temperature remains constant throughout the process, it follows from the theory of heat engines (Chap. IX) that the total work done by the working substance, *i.e.*, the area of the enclosed curve is zero. Hence the two areas $abca$ and $cdec$, since they are described in opposite senses, must be equal.

The maximum and minima points on the theoretical curve can be obtained by putting $\frac{\partial p}{\partial V} = 0$. Hence from (7), by differentiation,

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0, \quad . \quad . \quad . \quad (8)$$

or

$$T = \frac{2a(V-b)^2}{RV^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is also a cubic equation. Hence, for every isothermal there are three real or one real and two imaginary points of maxima or minima. The curves below P in Fig. 3 are seen to possess one maxima and one minima point while those above it have none at all. A slight mathematical transformation will show that the other point of minima lies in the region $V<b$ and hence has no physical meaning. Equations (7) and (9) when combined yield

$$p = \frac{a(V-2b)}{V^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This is the curve passing through the maxima and minima points and is shown by the dotted curve QPR.

In Fig. 2 all isothermals lower than P cut the dotted curve BB′PC′C at two points and, therefore, liquefaction can be observed by changing the volume along them. For the critical isothermal, *i.e.*, the isothermal corresponding to the critical temperature, these two points have coalesced into one. Referring to Fig. 3, it is readily seen that the isothermal passing through the point P, where P is a point of inflexion for the family of curves or a maxima point for the dotted curve, is the critical isothermal because below P every isothermal has got maxima and minima points while above P there are none at all. As we have seen above, if the isothermal has got maxima and minima points there must be liquefaction of the gas and we can find out the position where liquefaction begins. For liquefaction there must be two points on the curve having equal pressure. The highest isothermal for which this condition is satisfied is the one passing throug the point P since at P the maxima and minima points have coalesced into one. Hence P in Fig. 3 must be identified with the critical point and the isothermal through it with the critical isothermal. Now for P to be the maxima point of the dotted curve we have, by differentiating (19) with respect to V and equating to zero,

$$\frac{a}{V^3} - \frac{3a(V-2b)}{V^4} = 0$$

or $\qquad V_c = 3b.$

From (10) $\qquad p_c = \frac{a}{27b^2}$ $\qquad . \quad . \quad . \quad . \quad (11)$

and from (7) $\qquad T_c = \frac{8a}{27Rb}$

The critical constants may be very easily deduced from (7), since for the critical isothermal the point P is a maximum point as well as a point of inflexion, and for it both $\frac{\partial p}{\partial V}$ and $\frac{\partial^2 p}{\partial V^2}$ are equal to zero. We have therefore

$$\frac{\partial d}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0. \quad . \quad . \quad . \quad (8)$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0. \quad . \quad . \quad . \quad (12)$$

Combining (8) and (12) we get $V_c = 3b$, and then, with the help of (8), $T_c = \frac{8a}{27Rb}$. Finally from (7), $p_c = \frac{a}{27b^2}$ and $\frac{RT_c}{p_c V_c} = \frac{8}{3}$.

7. Defects in van der Waals' Equation.— In spite of general agreement deductions from van der Waals' equation show considerable deviation from experimental results. We have already shown that for carbon dioxide the curves drawn from van der Waals' equation do not quite agree with the experimental curves of Andrews. A particular isothermal may be made to agree much more closely with suitably chosen values of 'a' and 'b' but then for the same values the agreement is not so good for other isothermals. This only implies that 'a' and 'b' vary with temperature as has been directly found from experiments but van der Waals' theory assumes them to be constant. This is a great defect of the theory.

Another discrepancy however, lies in the value of the critical coefficient RT_c/p_cV_c. From equation (1) this should be 8/3 for all gases, independent of their nature. Actually, however, it varies from gas to gas, the value ranging from 2·25 for neon to 4·99 for acetic acid. It thus seems to depend upon the molecular structure of the gas.

Again van der Waals' equation gives $V_c=3b$, while experimentally it is found that V_c is more nearly equal to $2b$.

8. Experimental Study of the Equation of State.—The methods of determining isothermals for gases and liquids fall into two classes: (a) In the one, we observe the change in volume when different pressures are applied. (b) In the other, volume remains constant, the quantity of matter being varied.

(a) *Apparatus based on the principle of variable volume.*—When the pressure is small, the apparatus is quite simple and is given in elementary text-books as the Boyle's law apparatus. For higher pressures up to 100 atm. an apparatus due to Cailletet is used. This is described here. The same apparatus with certain modifications has been used by Regnault, Andrews and Amagat in their researches.

The apparatus is shown in Fig. 4. *T* is the measuring vessel made of stout glass which ends in a carefully calibrated capillary tube. The lower part of the vessel is placed in a steel cylinder. By means of a brass piece A and a screw E the vessel is held in the steel cylinder. M is a thermostat surrounding the upper narrow part of the tube which is again closed by means of a mantle C. The vessel T is filled with the gas under investigation at atmospheric pressure, the space between T and the inner wall B being filled with a sufficient quantity of mercury over which a quantity of glycerine or paraffin oil is poured. Pressure is communicated from a compression pump through glycerine to the measuring vessel. At high pressures mercury will rise up to the capillary tube and the volume can be easily read off from the calibration. When the pressure is high, it is measured by a compression manometer. If the pressure is above 300 atm. and is exerted only from the inside the capillaries are generally smashed, hence the experimental tube should be subjected to pressure from all sides. Such a pressure tube was built by Amagat.

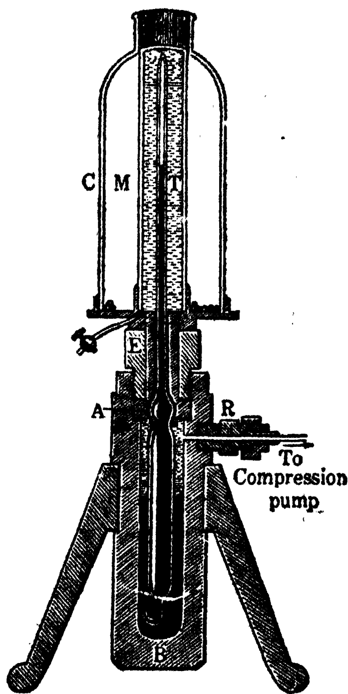


Fig. 4.—Cailletet's apparatus.

Amagat carried out an exhaustive study of the behaviour of several gases by the above method. In one set of experiments he employed pressures up to 450 atm., while in the next series pressures as high as 3,000 atmospheres were used.

(b) Apparatus based on the principle of variable mass.—This method was employed by Holborn and Schultze, Holborn and Otto and Kamerlingh Onnes. These investigators worked at high pressures and obtained important results. Since with increasing pressure the volume becomes smaller, greater error would occur in reading the volume at high pressures. To avoid it, these investigators kept the volume constant and used different quantities of the gas whose masses were determined. The apparatus becomes somewhat complicated by the presence of devices for the introduction and removal of the gas both inside and outside the

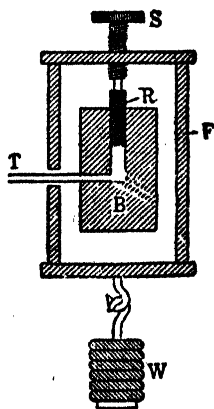


Fig. 5.—The pressure balance.

experimental vessel. An ingenious pressure balance shown in Fig. 5 was used to measure such high pressures. The metal block B was firmly clamped in position and carried the tube T which was connected to the apparatus containing the experimental gas. The block B has also a cylindrical hole in which the cylindrical rod R accurately fitted. Between R and the gas in the tube T there was castor oil so that gas pressure, transmitted through the oil, tended to raise the piston R. This was just prevented by the screw S pressing on the top of R with the combined weight of the frame F and weights W. When balance is obtained, *i.e.*, the piston neither rises nor falls, the gas pressure $p = mg/a$, where m is the mass of R, S, F, and W, and a is the cross-section of the piston or the cylinder.

9. Discussion of Results.—Amagat represented his results by graphs in which pV denotes the ordinate and p the abscissa. The curves for hydrogen and nitrogen for several temperatures are shown in Fig. 6. As already mentioned, for hydrogen the product pV increases with pressure, but for nitrogen it first decreases. The curves are straight lines *inclined* to the pressure axis, while if Boyle's law were true, they would be straight lines parallel to the pressure axis. The curves for carbon dioxide (Fig. 7) are typical of all gases. The isothermals below about 30° have a portion of them parallel to the pV-axis. This indicates that the pressure remains constant while the volume varies, and corresponds to the condensation of the vapour. Further, it is seen that the curvature of the isothermals diminishes as the temperature rises. The minima points on isothermals gradually recede away from the origin, and the dotted curve through them is parabolic. At still higher temperatures no minima point is found and carbon dioxide behaves like hydrogen.

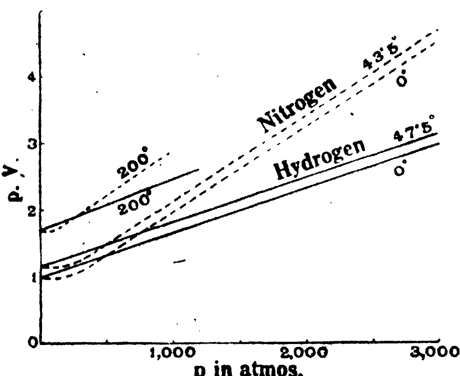


Fig. 6.—Amagat's curves (*PV against p*) for different gases.

This general behaviour of the isothermals can be easily explained from van der Waals' equation. We have

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT,$$

or

$$pV - pb + \frac{a}{V} - \frac{ab}{V^2} = RT. \quad . \quad . \quad . \quad (13)$$

In the third and fourth terms which are small, we can make the approximate substitution $V = RT/p$. Eqn. (13) then yields

$$pV - pb + \frac{ap}{RT} - \frac{abp^2}{R^2T^2} = RT. \quad . \quad . \quad . \quad (14)$$

At high temperatures the term abp^2/R^2T^2 can be neglected. If we then plot pV as y-coordinate and p as x-coordinate, the plot will be a straight line inclined to the pressure axis (e.g. curves for H_2 in

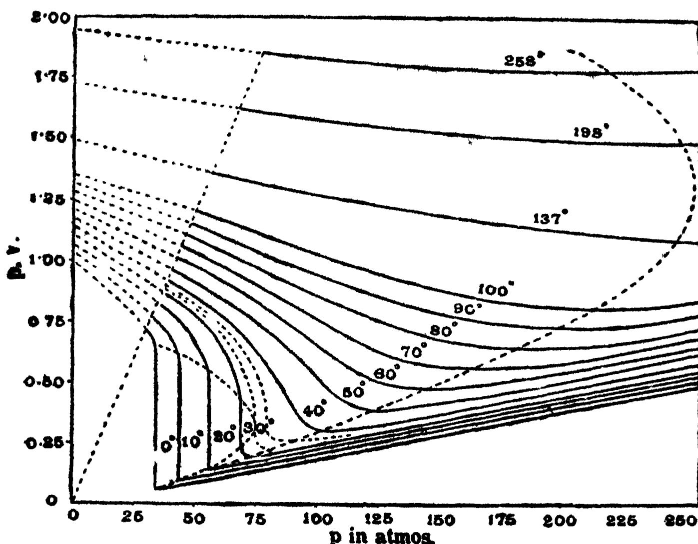


Fig. 7.—Curves for carbon dioxide.

Fig. 6). Thus for temperatures above the Boyle point $T_B = a/bR$ the slope will always be positive as for H_2 in the figure. For temperatures below the Boyle point as in the case of N_2 and CO_2 in Figs. 6 and 7, the slope will be negative unless the pressure is too high. This can be readily seen from eqn. (14) which holds for the general case, since

$$\text{slope} = \frac{\partial y}{\partial x} = b - \frac{a}{RT} + \frac{2abp}{R^2T^2}. \quad . \quad . \quad . \quad (15)$$

The slope is therefore negative at low pressures but becomes positive at sufficiently high pressures. The minima point on the Amagat curves *i.e.*, the point where the slope changes its sign, can be obtained by equating (15) to zero. Thus corresponding to any single value of pressure there are two temperatures given by the relation

$$b - \frac{a}{RT} + \frac{2abp}{R^2T^2} = 0, \quad . \quad . \quad . \quad . \quad (16)$$

i.e., the dotted curve through the minima points is approximately parabolic. Eqn. (16) shows that the dotted curve will meet the axis $p=0$ at the Boyle temperature $T_B = a/bR$. Thus Amagat's curves can be fully explained with the help of van der Waals' equation.

10. Experimental Determination of Critical Constants.—We have defined the critical constants in sec. 8. They are constants characteristic of every substance, and are of fundamental importance as they occur in certain equations of state. Their importance in the study of liquefaction is discussed in Chapter VI.

The determination of these critical values is often a task of considerable difficulty. Of these the *critical temperature* is the easiest to measure accurately. For ordinary substances* a hard glass tube like that of Andrews and connected to a manometer may be employed. Sufficient quantity of the liquid is introduced and the tube surrounded by a thermostat which can be maintained at constant temperatures differing by very small amounts. The temperatures at which the liquid suddenly disappears and reappears are observed, the mean of these giving the critical temperature. The *critical pressure* is the pressure at the critical temperature and can be read easily from the manometer. The *critical volume* is much more difficult to measure accurately, for even a small variation of temperature by 0·1°C produces a large change in volume, and hence the substance has to be kept exactly at the critical temperature. The pressure must also be exactly equal to the critical pressure since the compressibility of the substance in this region is very great. The method adopted was to arrange in such a way that a very slight increase of volume lowered the temperature by a small amount and caused the separation of the mass into liquid and vapour, the liquid appearing at the top. This initial volume is called the *critical volume*. The amount of substance initially contained in the tube has thus to be adjusted.

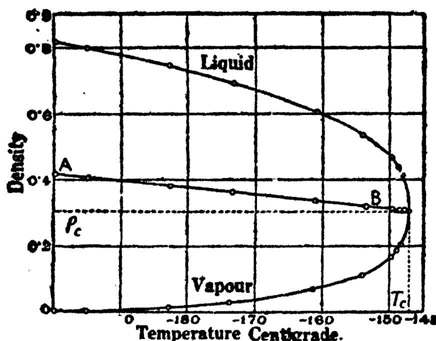


Fig. 8.—Law of Rectilinear Diameters.

The most accurate method, however, is to make use of the *Law of Rectilinear Diameters* or mean densities, discovered by Cailletet and Mathias. If the density of a liquid and of its saturated vapour be represented by ordinates and the corresponding temperatures by abscissae, a curve roughly parabolic in shape is obtained (Fig. 8). In the figure the vapour density of nitrogen is plotted from the observations of Onnes and Crommelin and is typical of all substances. The densities in the two states go on approaching each other till they become equal at the critical tempera-

* Sometimes a simple apparatus, first suggested by Cagniard de la Tour is employed for the purpose. It consists of a glass tube shaped like J, with its shorter arm somewhat broadened and containing the liquid in question which is separated from air in the larger arm by a column of mercury. The two ends are closed, the air in the longer arm serving as a compression manometer. The disappearance of the surface of separation between the liquid and its vapour in the shorter arm was observed.

ture. The curve AB is a line passing through the mean of the vapour and liquid densities and will consequently pass through the critical temperature. It was first observed by Cailletet and Mathias that for all substances this line was straight or very nearly so. The equation for this line is $y=\frac{1}{2}(\rho_l+\rho_v)=a+bt$ where y is the ordinate and t the abscissa and ρ_l, ρ_v denote the densities in the liquid and the vapour states respectively. This law enables us to find the critical density or the critical volume, for we determine the densities of the saturated vapour and the liquid as near to the critical temperature as possible, then draw the rectilinear diameter. The intersection of this line with the ordinate at the critical temperature gives the critical density ρ_c or the critical volume.

For substances like water which attack glass at high temperatures Cailletet and Colardeau employed the apparatus shown in Fig. 9. The strong steel tube AB, platinized inside to prevent attack, contains the water or the substance to be investigated. It is immersed in a temperature bath LL which is heated by a gas regulated burner,

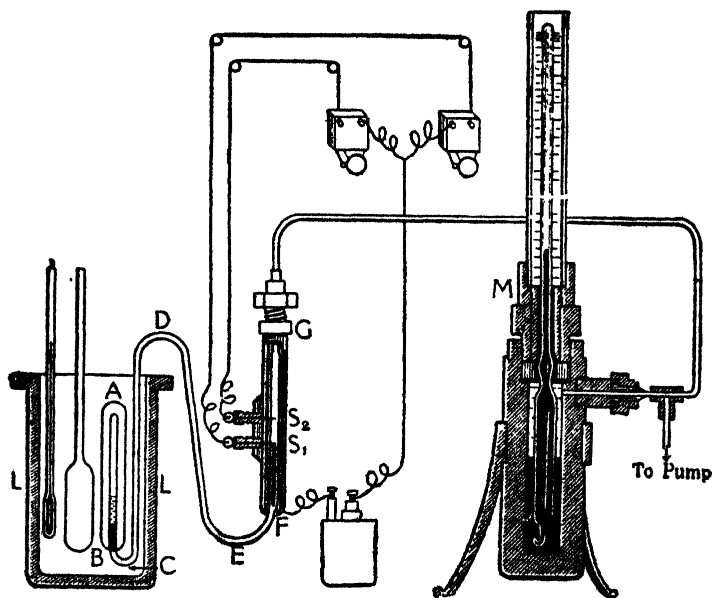


Fig. 9.—Cailletet and Colardeau's apparatus.

and thus its temperature can be kept constant. The tube AB is connected to a similar steel tube FG by means of the flexible steel spiral CDE. Mercury fills part of the tube AB, the spiral CDE and the tube FG up to the level S_1, above which there is water filling the entire tube up to the manometer. Different pressures can be applied by the force pump as indicated. At S_1 an insulated platinum wire which is sealed in the side of the wall completes an electric bell circuit. When the temperature of the bath is raised the pressure of

the vapour in OB rises, mercury is forced past S_1 in FG and sets the bell ringing. Water is forced in by the pump to keep the level of mercury constantly at S_1 and thus the volume occupied by the water and water vapour in AB remains constant. The platinum wire at S_2 completes another electric circuit and serves to sound a warning that the whole mercury is about to be expelled out of AB.

We thus get the vapour pressure curve of the substance. The curve is perfectly continuous and characteristic of the substance. For water this is shown in Fig. 10. If, however, we start with different quantities of the liquid we get the same curve as far as M, but above it we get different curves. The vapour pressure thus appears to branch off at M, a point whose position was found by Cailletet to be practically independent of the quantity of liquid taken. This temperature is the critical temperature for the substance.

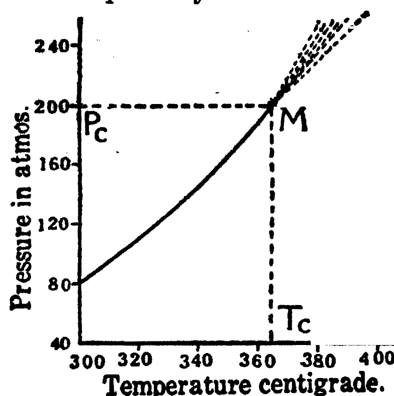


Fig. 10.—Vapour Pressure Curve for Water.

11. We give below a table of critical constants, taken from Landolt and Bornstein's *Physikalisch-Chemische Tabellen.*

Table 2.—Critical data.

Gas	T_c in °C.	p_c in atm.	v_c Specific volume	$\frac{RT_c}{p_cV_c}$
Helium ..	—267·9	2·25	15·4	3·13
Hydrogen ..	—239·9	12·8	32·2	3·28
Argon ..	—122·9	48·0	1·88	3·43
Oxygen ..	—118·8	49·7	2·32	3·42
Nitrogen ..	—147·1	33·5	3·21	3·42
Carbon-dioxide ..	31·0	72·8	2·17	3·48
Ammonia ..	132·2	112·3	4·24	4·12
Ether ..	193·8	35·6	3·85	3·81
Sulphur dioxide ..	157·2	77·6	1·95	3·60
Methyl chloride ..	143·1	65·9	2·71	3·80
Water ..	374·2	220	2·6	

12. Matter near the Critical Point.— There has been much discussion about the state of matter near the critical point since the time of Andrews. The properties actually observed are:—(1) the

densities of the liquid and the vapour gradually approach each other till they become equal at the critical point; (2) at the critical temperature the boundary line between the liquid and the vapour disappears, and hence there must be mutual diffusion, and the surface tension must vanish, *i.e.*, the molecular attraction in the liquid and vapour states must become equal ; (3) the whole mass presents a very flickering appearance which suggests that there might be variations of density inside the mass. This was experimentally observed to be so by Hein and others. They suspended spheres of different densities inside the fluid when each comes to rest at a horizontal surface having a density equal to its own ; (4) compressibility of vapour at the critical point is infinite and is very great near that point. As pointed out by Guoy, this explains the variation of density throughout the mass observed in (3), for the superincumbent vapour causes the density of lower parts to increase.

From these considerations the simplest and probably the most correct view which was put forward by Andrews appears to be that just beyond the critical temperature the whole mass is converted into vapour consisting of a single constituent and should behave like a gas near its point of liquefaction.

According to this theory the critical phenomenon, *i.e.*, the disappearance of the boundary between the liquid and the vapour and not its motion, should occur only when the amount of liquid in the tube is such that it will fill the whole tube with vapour of critical density. If more liquid is present the meniscus should go on rising till at the critical temperature the whole tube becomes filled with liquid. If less liquid is present, the meniscus goes on falling till at the critical temperature the whole should become filled with vapour alone. Experimentally, however, Hein found that the critical phenomenon is observable when the initial density varies from 0·735 to 1·269 times the critical density. This is probably due to the property (4) as the variation of density inside the mass allows the excess or deficit amount to be adjusted. The branching of the vapour pressure curve at M observed by Cailletet and Colardeau may be explained in a similar way.

Experiments with water by Callendar point to the existence of a critical region rather than a critical point. He found that the density of the liquid and the vapour did not become equal at the temperature at which the meniscus disappeared, but that a difference of density was perceptible even beyond that temperature. The critical point is that point at which the properties in the two phases become equal.

Books Recommended.

1. Jeans, *Kinetic Theory of Gases*, C. U. P. (1940)
2. Kennard, *Kinetic Theory of Gases*, (1938).
3. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1.

CHAPTER V

CHANGE OF STATE

FUSION—VAPORISATION—SUBLIMATION

1. It is a matter of common experience that on the application of heat, substances change their state of aggregation. Thus when ice is heated it melts into liquid (water) at 0°C (the melting point). When further heated the liquid passes completely into the vapour state at 100°C (the boiling point) under atmospheric pressure. Conversely, on withdrawing heat from a gas, it liquefies at the liquefaction point and later the liquid solidifies at the freezing point or solidification point. For a pure substance the melting and the freezing points are identical, as are also the boiling and the liquefaction points.

The temperature at which any change of state takes place is generally fixed provided the external pressure is fixed and the substance is pure. The fusion point usually varies very little with the pressure (it requires a pressure of about 130 atm. to lower the melting point of ice to -1°C), but the variation of the boiling point with pressure is very great. As a matter of fact, it can be easily shown that water can be made to boil at any temperature up to 0°C.* provided the pressure is sufficiently reduced. Conversely, the boiling point can also be raised considerably if the pressure be sufficiently increased. These facts can be readily verified by considering evaporation in a closed space.

2. Evaporation in a Closed Space.—If we fill a glass vessel partly with water and evacuate it with a pump, then water will begin to boil even at room temperature. If the pump be now cut off, the pressure can be measured by a manometer. For a certain definite temperature of the liquid, there is always a definite vapour pressure. If we increase the total space, more liquid will evaporate and fill up the extra space. If we reduce the space, some vapour will condense till the remaining vapour exerts the same pressure. If there is a third gas, not reacting with the vapour, the partial pressure of the liquid will be approximately equal to the vapour pressure in the absence of the third gas. It is an important experimental task in Physics to determine the vapour pressure of a liquid at different temperatures.

3. Latent Heat.—Black found that the change from one state to another is not abrupt, but a large amount of heat must be absorbed before the entire mass is converted from one state to another at the same temperature.† Thus to convert 1 gram of

* More rigorously, up to the triple point.

† We have already discussed in Chap. II, pp. 33-37, the methods of measuring quantity of heat by Change of State.

ice at 0°C to 1 gram of water at 0°C, about 80 calories of heat are required. The amount of heat required to convert 1 gram of a solid into a liquid without raising the temperature is called the *latent heat of fusion*. This amount of heat is required for overcoming the forces of attraction between the particles of the solid, so that they may become mobile enough to form a liquid. In solids the molecules are imagined as vibrating about mean equilibrium positions which are fixed but in liquids they execute rotational and translational motions and wander throughout the liquid, though considerably hampered. Similarly, to convert one gram of water at 100°C to vapour at 100°C, 538·7 calories are required. This heat, which is necessary, for pulling the molecules of water so far apart that they become quite independent of each other (vapour state) is known as the *latent heat of vaporisation*. It will be seen that the latent heat varies greatly with the temperature of vaporisation.

4. Sublimation.—Sometimes a solid may pass to a vapour state without passing through the intermediate liquid state. Camphor furnishes a good example of this class. On being heated it does not melt, but simply evaporates. Such a process is called *sublimation* and the substance is said to be volatile.

But we shall see that the process is not peculiar to any particular substance. All solid substances possess finite vapour tension at even ordinary temperature. When this vapour tension is too small, we take no notice of it, but with the aid of delicate apparatus, it can be measured. A substance is said to be *volatile* only when the boiling point at atmospheric pressure is less than the melting point. Thus under an atmosphere different from our own, say at the moon, even ice which we do not consider volatile would have to be treated as such. The moon is supposed to have a very thin atmosphere (<1 mm. of mercury), and the temperature is below 0°C. If we consider ourselves transported to the moon, our studies will show that ice is volatile because on being heated, it will evaporate to the gaseous state without passing through the liquid state. If we want liquid water in the moon we must artificially produce a high pressure and apply heat to ice under this pressure. Similarly, camphor can be melted to a liquid form when it is heated under high pressure.

5. Amorphous Solids.—Impure substances, mixtures, and non-crystalline substances do not usually have a sharp melting point; in their case fusion and solidification take place over a short range of temperature. This is due to the presence of two or more substances which do not solidify at the same temperature. Examples of such amorphous substances are wax, pitch, glass etc. Glass gradually softens throughout its bulk as its temperature is raised and is usually regarded as a supercooled liquid.

6. Change of Properties on Melting.—Several properties of substances change in a very marked way when a substance melts. This is due to the regular arrangement of the molecules in the solid being destroyed by the addition of heat. The following are some of these properties :—

(1) *Change of Volume.*—Most substances expand on solidification while a few others contract. To the former class belong ice, iron, bismuth, antimony, etc.; paraffin wax and most metals belong to the latter class. Good castings can only be made from substances of the former class. Often enormous force is exerted by water when it freezes into ice. The bursting of water pipes and of plant cells and the splitting of rocks is due to this cause.

(2) *Change of Vapour Pressure.*—The vapour pressure abruptly changes at the melting point. The vapour pressure curves of the solid and liquid states are different and there is a sharp discontinuity at the melting point (Chap. X, § 41).

(3) *Change of Electrical Resistance.*—The electrical resistance of metals undergoes a sudden change on melting. When the substance contracts on melting the conductivity increases and when it expands on melting the conductivity decreases. Table 1* below gives the ratio of the resistance of the fluid metal to that of the solid form at the melting point for a number of metals.

Table 1.

The Ratio $\dfrac{\textit{resistance of fluid metal}}{\textit{resistance of crystallised metal}}$ *for some metals.*

Substance	Ratio	Substance	Ratio
Al	1·65	Cu	1·97
Sb	0·70	Li	1·96
Pb	2·0	Na	1·34
Cd	1·97	Ag	1·98
Cs	1·65	Bi	0·45
Ga	0·58	Zn	2·00
Au	2·28	Sn	2·01
K	1·32		

(4) It is also found that molten metals show a discontinuity in their dissolving power at the melting point.

7. Determination of the Melting Point.—The melting point under normal conditions can be determined with very simple apparatus. The substance may be heated in a crucible electrically or otherwise. For high temperatures, the crucible must be of graphite or some other suitable material, and the substance heated in a non-oxidizing atmosphere. If the substance is rare, it can be employed in the form of a wire (wire-method). As thermometer, the secondary standards are very convenient to use, the thermo-couple or the

* Taken from *Handbuch der Physik*, Vol. X, p. 37.

resistance thermometer being generally chosen ; such thermocouples or resistance wires must not be thrust directly into the melting substance, but should be protected by a sheath of protecting material, say porcelain, hard glass or magnesia tubes. Now as long as the substance is melting the temperature remains constant and hence the E.M.F. of the thermo-couple or the resistance of the thermometer is also stationary. A curve is plotted with the E.M.F. or the resistance as ordinate and time as abscissa. The horizontal part represents the freezing of the metal and the corresponding E.M.F. gives its melting point. Such a curve for copper is shown in Fig. 1 where 90Pt-10Rh, Pt couple is used. The constant E.M.F. corresponding to the horizontal part is about 10·5 mV, which corresponds to 1084°C.

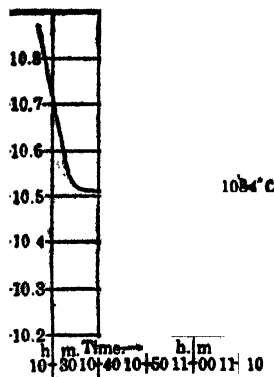


Fig. 1.—Melting point of copper.

8. Determination of the Latent Heat of Fusion.—For determining the latent heat of fusion, an ordinary calorimetric method (Chap. II) may be employed, *e.g.*,—(1) the method of mixtures, (2) the Bunsen ice calorimeter, (3) the method of cooling, and (4) electrical methods. Method (3) is unimportant and will not be considered here.

The method of mixtures.—It is quite simple and has been explained in Chap. II. Most of the early determinations of the latent heat of ice were made by this method. Thus if M grams of ice at 0°C are added to a calorimeter containing water whose total thermal capacity is W and initial temperature θ_1 and if θ_2 be the final temperature, the latent heat L is given by the relation

$$ML+M\theta_2 = W(\theta_1-\theta_2). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

An important source of error in the above method lies in the fact that some water adheres to the crystals of ice at 0°C. To eliminate this, ice below 0°C is frequently chosen which requires a knowledge of the specific heat of ice. In this method we are required to find the heat taken up by ice in being heated. A converse method may also be employed, *viz.*, the heat given out by water in solidification may be found. The most accurate experiments give the value L=79·6 cal. for the latent heat of fusion of ice.

The method of mixtures has been very conveniently adopted to the simultaneous determination of the melting point and the latent heat of fusion of metals and their salts. Goodwin and Kalmus employed this method for finding the latent heat of fusion of various salts. A known weight of the substance contained in a sealed platinum vessel is heated in an electric furnace to a high accurately measurable temperature. It is then dropped into a calorimeter and the quantity of heat liberated is determined in the usual manner. The electric furnace

is specially designed to secure a uniform temperature throughout the platinum cylinder which is measured by a Pt-Rh thermo-couple. As calorimetric liquid, water was employed below 450°C and aniline above that temperature.

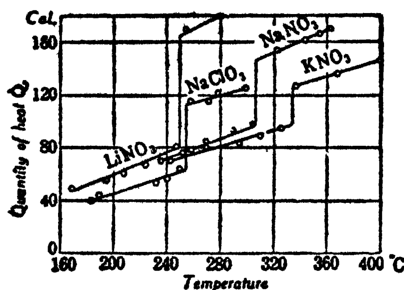


Fig. 2.—Latent Heat of Fusion of Salts.

First a blank experiment gives the heat capacity of the platinum vessel. The experiment is then performed with the substance heated to different initial temperatures extending over a range of about 50°C both above and below the melting point, and the final temperature of the calorimeter noted. From these after correcting for the heat capacity of the vessel, the quantity of heat Q necessary to raise 1 gram of the substance from the room temperature to its initial temperature could be calculated. Plotting Q as ordinate and T the corresponding initial temperature as abscissa curves of the type shown in Fig. 2 are obtained. The discontinuity in the value of Q indicated by the vertical line gives the latent heat of fusion, the temperature at which this discontinuity appears is the melting point T_m, and the slope of the curve at any temperature gives the specific heat of the substance at that temperature.

This method has been considerably improved by Awbery and E. Griffiths who have made accurate determination of the latent heat of fusion of several metals. They employed a very special type of calorimeter which was so designed that the heated substance could be kept surrounded by water inside the calorimeter and the lid of the latter closed before any water had access to it, so that the loss of liquid by evaporation was eliminated.

Electrical Method.—This consists in measuring the amount of electrical energy required to heat a mass of the substance below its melting point to a temperature above it. The method was employed by Dickinson, Harper and Osborne for finding the latent heat of fusion of ice. Electrical energy was supplied to a special calorimeter similar to that of Nernst in which ice below 0°C was placed. Then

$$E = \int_{T_1}^{T_m} c_{p1}\, dT + L + \int_{T_m}^{T_2} c_{p2} dT, \qquad . \qquad . \quad (2)$$

where E denotes the electrical energy supplied per gram, T_1, T_2 its initial and final temperatures and c_{p1}, c_{p2} the specific heats of ice and water respectively. From this relation L can be calculated. This method is very convenient for finding the latent heat at low temperatures.

Methods similar to the foregoing can also be employed for finding the heat of transformation of one allotropic modification to another but we are not concerned with them here.

9. Indirect Method.—Another method of finding the latent heat consists in making use of the Clausius-Clapeyron relation (Chap. X)

$$L = T\frac{\partial p}{\partial T}(v_2 - v_1), \qquad (3)$$

where v_2, v_1 denote the specific volumes of the liquid and solid respectively, and $\frac{\partial p}{\partial T}$ the ratio of the change of pressure to the change of the freezing point. In this way L can be easily found.

10. Empirical Relationships.—It was observed by Richards that if ML denotes the latent heat multiplied by the atomic weight and T_m the melting point, ML/T_m is approximately constant for all substances and its value lies between 2 and 3. This generalisation is known as *Trouton's Rule*. But the relation is only approximately true, and the value of the constant seems to depend upon the nature of the crystalline form in which the substance solidifies. Table 2* shows how far this generalisation holds.

Table 2.—Illustration of Trouton's Rule

Substance	Atomic latent heat in cal.	Melting point T_m	$\frac{ML}{T_m}$	Crystal system
Na	630	371	1·7	Body-centred cube
K	570	336	1·7	
Rb	520	312	1·7	
Cs	590	300	1·7	
Cu	2750	1356	2·03	Face-centred cube
Ag	2630	1234	2·13	
Au	3100	1337	2·32	
Pb	1170	600	1·96	
Al	2500	930	2·70	
Mg	1130	927	1·22	Hexagonal.
Zn	1800	692	2·60	
Cd	1500	594	2·53	
Hg	560	234	2·40	

11. Effect of Pressure on Melting Point. Regelation.—As already mentioned the melting point of a substance is not quite fixed; it changes when the external pressure is varied. Equation (3) giving the change in melting point due to pressure has been deduced in Chap. X from thermodynamic considerations. This expression clearly shows that the melting point of substances which expand on solidification is lowered by increase of pressure while the converse is the case for the other class of substances.

* Largely taken from *Handbuch der Experimental-physik*, Vol. 8, Part I, p. 592.

Ice belongs to the first category. It is this property of ice which accounts for the well-known phenomenon of *Regelation*, *i.e.*, the melting of ice under pressure and its resolidification when the pressure is released. This property enables us to explain the elegant experiment of Tyndall* in which a piece of wire loaded at either end with weights and placed on a block of ice finds its way through the latter though the latter remains intact. The well-known phenomenon of glacier motion is partly due to the same cause. Snow goes on depositing on a mountain and when the mass attains sufficient height the ice at the bottom melts under pressure and begins to flow, but as soon as the pressure is released it resolidifies. The block of ice thus continuously shifts down the slope and we have the phenomenon of glacier motion.

12. Fusion of Alloys.—Alloys, except those having composition in the neighbourhood of that of the eutectic alloy, do not have a definite melting point. Consider for example an alloy of lead and tin. The melting point of lead is 327°C and that of tin is 232°C, the eutectic alloy having the composition 63% Sn and 37% Pb. If an alloy of 90% Sn and 10% Pb is cooled from the molten state it first becomes pasty at about 210°C when solidification commences and tin begins to separate out, and this continues till a temperature of 183°C is reached and the remaining liquid mass which has the composition 63% Sn and 37% Pb solidifies completely. Thus the addition of a little lead to tin or a little tin to lead has the effect of lowering the melting point of the pure substance just as the addition of a little salt lowers the melting point of ice. In fact the behaviour of the alloy is just like that of the salt solution depicted in Fig. 1, Chap. VI.

Similarly if we start with a molten alloy rich in lead *i.e.*, 80% Pb 20% Sn, the mass first becomes pasty at about 275°C when lead begins to separate out and finally the whole mass solidifies at 183°C. Thus whenever the alloy is very rich in one component, the molten mass will first become pasty on cooling, the paste consisting of crystals of solid held in the liquid, and this will be indicated by a halt in the cooling curve. On further cooling a second halt is reached when the entire mass solidifies at 183°C. The alloy corresponding to the composition 63% Sn 37% Pb is called the eutectic alloy and this temperature of 183°C is called the eutectic temperature. If we start with the alloy of this composition it will solidify or melt at a definite temperature—the eutectic temperature. Similarly if we melt an alloy of composition other than the eutectic, it will first become pasty and then at a higher temperature melt completely. The alloys of other metals in general behave similarly.

Alloys are of considerable practical importance. Thus ordinary soft solder or tinman's solder is an alloy of lead and tin having about 60% Sn *i.e.* a eutectic mixture of lead and tin. It has a melting

* John Tyndall (1820–1893). Born in Ireland, he studied at Marburg and in Berlin. From 1853 onwards he was Professor of Physics at the Royal Institution in London. He was well-known as a brilliant experimenter and was fond of mountaineering.

point much lower than that of tin or lead, and has a sharp and definite temperature of solidification. An alloy of tin and lead (tin, 5; lead, 1) melts at 194°C; Rose's fusible metal (tin, 1; lead, 1; bismuth, 2) melts at 94°C; Wood's fusible metal (tin, 1; lead, 2; cadmium, 1; bismuth, 4) melts at 60·5°C though the melting points of bismuth, lead and tin are 269, 327, 232°C respectively.

13. Supercooling.—It has been stated above that when a liquid is cooled it solidifies at a definite temperature (its freezing point). Most liquids, however, if slowly cooled in a perfectly clean vessel, can be brought down to a temperature much below the normal freezing point without solidifying. This is known as the phenomenon of *supercooling* or surfusion. Water can in this way be cooled down to −10°C or still lower with a little care. Dufour suspended a minute drop of water in a mixture of chloroform and of sweet almonds which had a specific gravity equal to that of the water drop and managed to cool the latter to −20°C without solidification while a drop of naphthalene could be supercooled to 40°C (normal melting point being 80°C).

Supercooling is, however, essentially an unstable phenomenon. The introduction of the smallest quantity of the solid in which the liquid would freeze at once starts the solidification. Mechanical disturbance such as shaking the tube, stirring or rubbing the sides with a glass rod, or addition of some other solid is often sufficient to start solidification. If solidification has once started it will continue with evolution of heat till the normal freezing point is reached. After that further solidification will take place only when heat is lost by radiation, etc. Absence of air favours supercooling probably because the dust particles contained in it are then absent.

VAPORISATION

14. Evaporation, Boiling and Superheating.—A substance can pass from the liquid state to the vapour state in two ways, *viz.* (i) evaporation and (ii) ebullition or boiling. In the former the formation of vapour takes place slowly at the surface at all temperatures, while in the latter the vapour is formed in all parts of the liquid at a constant temperature and escapes in the form of bubbles producing a hissing noise. Initially these vapour bubbles are formed around small bubbles of air clinging to the bottom and sides of the vessel which facilitate the process of boiling. If, however, the liquid is carefully freed from dissolved air and then heated in a clean vessel, its temperature can be raised several degrees above 100°C without its beginning to boil, but when boiling starts due to disturbances of any kind, it starts with explosive violence, usually called bumping, and the temperature falls to 100°C. This *superheating* is the cause of bumping and is prevented by the addition of porous objects.

15. Saturated and Unsaturated Vapours.—If the vapour escaping from a liquid either by evaporation or by boiling is collected in a vessel it will form an unsaturated vapour. In the case of evaporation in a closed space as in §2, the space will be filled with un-

saturated vapour if all the liquid has evaporated, but if the vapour remains in contact with some liquid, it will be saturated. Unsaturated vapour approximately obeys Boyle's law but for saturated vapour the pressure depends only the temperature and not on the volume. When saturated vapour is heated it becomes unsaturated or superheated. When saturated vapour is cooled without condensation occurring it becomes supersaturated.

We shall now describe some methods for determining the vapour pressure. The range of pressure to be measured varies from 10^{-4} mm. to 400 atmospheres. In certain cases, pressures as low at 10^{-6} mm. have to be measured. It is clear that such wide range of values requires various kinds of apparatus.

16. Vapour Pressure of Water.—The first accurate determination of the pressure of saturated vapour was made by Dalton. A similar but improved apparatus was later employed by Regnault for finding the vapour pressure at temperatures lying between 0° and 50°C. Regnault's experiments were performed with the greatest care and extend over a wide range of temperatures. His apparatus for the range 0° – 50° is shown in Fig. 3. Two barometer tubes A and B were arranged side by side, fed from the same cistern of mercury M. The space *a* above the mercury level in the tube B is vacuum, while water is gradually introduced at the bottom of A till it rises through the mercury column and evaporates on reaching *b*. More water is introduced till a small layer remains floating over the mercury surface in A. A constant temperature bath DD furnished with stirrer (not shown), and a thermometer surrounds *a*, *b*, as well as some length of the mercury column. The difference in the heights of the two mercury columns, which are observed through a glass window with a cathetometer, gives the saturated vapour pressure of water at the temperature of the bath. Correction must be made for the weight of water in B, for effects of capillarity, refraction, etc.

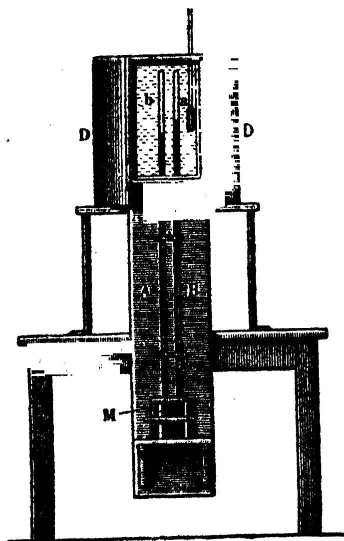


Fig. 3.—Regnault's vapour pressure apparatus.

For temperatures below 0°C Regnault modified his apparatus to that of Gay Lussac. The top of the tube A was bent round and terminated in a spherical bulb which contained water or ice and was surrounded by a suitable bath. For temperatures not much above 50°C the apparatus already described (Fig. 3) could be used when a

longer bath would be necessary, but Regnault preferred the boiling point apparatus (Sec. 18).

17. General Methods.—The methods used for measuring saturated vapour pressure can be broadly divided into two classes:

(*i*) Methods in which the temperature is kept fixed and the pressure is determined either manometrically or by measuring the density of saturated vapour. This is called the *direct* or *static* method.

(*ii*) Methods in which the pressure is given and the temperature at which the liquid begins to boil is determined. This is the *dynamic* method.

18. Statical Methods.—Regnault's method is illustrative of class (*i*). The same method can be adopted for finding the vapour pressure of any liquid provided it does not react with mercury and the vapour pressure is neither too high nor too low. A number of investigators have employed this method. Their apparatuses differ only in unessential details. A general scheme of apparatus utilising this method is shown in Fig. 4. A is a small glass sphere, a few c.c. in capacity, to which is attached a glass tube C and another glass tube D with a smaller bore. This is connected to a bigger globe G and a mercury manometer M about 90 cm. long. The whole apparatus is first evacuated through the stop-cock S_1 and then the latter is closed. Next the gas under investigation is introduced through the stop-cock S_2 and condensed in A by suitably cooling the latter ; finally S_2 is also closed. The sphere A is then surrounded by temperature baths and the vapour pressure corresponding to the temperature of the bath is indicated by the manometer M. B is a barometer to indicate the atmospheric pressure. The apparatus is convenient for measuring vapour pressures from a few cm. to the atmospheric pressure. For higher pressures a compressed air manometer may be employed when the whole apparatus has to be made of steel.

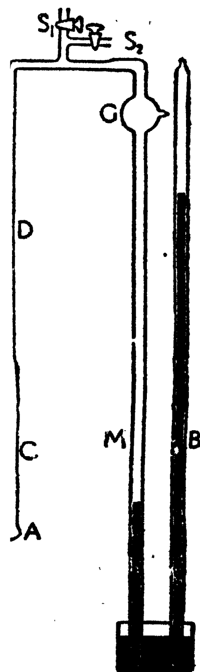


Fig. 4.—Determination of vapour pressure by statical method.

A similar apparatus was employed by Henning and Stock for finding the vapour pressure of a number of gases between +10 and −181°C. On the same principle Siemens has developed vapour pressure thermometry at low temperatures. For high pressures we may mention the classical experiments of Cailletet and Colardeau (p. 101) with water. Andrews' apparatus (p. 88) may also be used. Holborn and Baumann determined the vapour pressure of water above 200°C by the statical method. The method has also been employed by Smith and Menzies though their apparatus is much different.

In the experiment mentioned above the pressure was measured manometrically, but the pressure may also be found by determining the density of saturated vapour, for assuming that the perfect gas equation holds, we have

$$p = \frac{\rho RT}{M}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus knowing M, ρ we can calculate p. A very simple apparatus based on this method was employed by Isnardi and Gans. A portion of the vapour was isolated and its density determined.

19. Dynamical or Boiling Point Method.— This method is based on the fact that when a liquid boils, its vapour pressure equals the external pressure on the surface of the liquid. A definite external pressure is applied on the liquid surface by means of a pump and then the liquid is heated. The liquid will boil at the temperature at which its vapour pressure equals the external pressure, *viz.*, that set up by the pump. Hence the vapour pressure corresponding to the temperature of ebullition is the pressure exerted by the pump and can be read on a manometer.

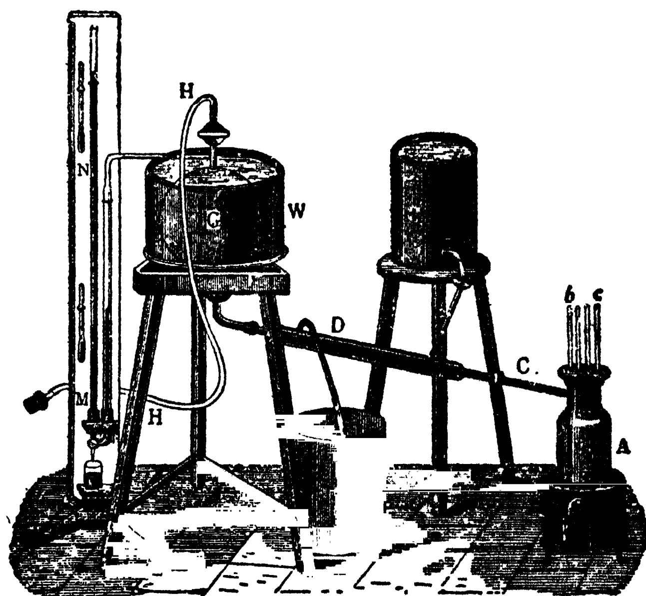


Fig. 5.—Regnault's Vapour Pressure Apparatus (Dynamical method.)

Regnault employed this method for finding the vapour pressure of water between 50°C and 200°C. His apparatus is indicated in Fig. 5. The copper boiler A is partly filled with the experimental liquid and contains four thermometers *bc* immersed to different depths inside the vapour and the liquid. The upper part of the boiler is

connected by means of H to a pump, the pressure being indicated by the mercury manometer NM. The reservoir is kept immersed in a water-bath W and serves to transmit the pressure from the boiler to the manometer as well as to smooth the fluctuations in the pressure maintained by the pump. The vapour of the liquid condenses in C and returns to the boiler, thus the same quantity of liquid is used over and over again. First, a definite pressure is established by the pump and the boiler heated. In a short time the readings indicated by the thermometers *bc* become steady. The manometer indicates the vapour pressure corresponding to this temperature.

The apparatus can be adapted for all pressures. For high pressure all the parts must be made of copper and the pump must be a force pump. The method is capable of great accuracy. By this method Holborn and Henning have very accurately determined the vapour pressure of water between 50 and 200°C ($\frac{1}{2}$ to 16 atm.). Ramsay and Young applied this method to the measurement of very small vapour pressures. Their apparatus (Fig. 6) consists of a wide glass tube T to which is connected a reservoir R, the latter being connected to an air pump and a manometer M. Definite pressure is set up by the pump and the experimental liquid, stored in F, is allowed to drop on the cotton wool surrounding the bulb of the thermometer. The tube T is kept surrounded by a sufficiently hot bath so that the experimental liquid at once evaporates inside T and the thermometer soon reaches a steady temperature, the true boiling point of the liquid under that pressure.

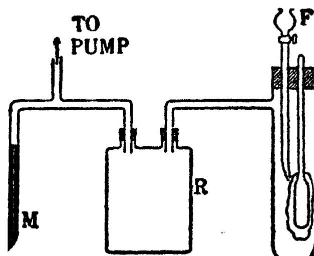


Fig. 6.—Ramsay and Young's apparatus.

Smith and Menzies have devised an ingenious modification of the boiling point method. Their apparatus is indicated in Fig. 7. The substance under investigation is kept in the sphere A close to the bulb of the thermometer T, both being immersed in some liquid contained in the test-tube B. The test-tube is closed airtight and communicates with a pump and manometer (not shown). It is further surrounded by a bath whose temperature can be varied. A definite pressure is first established by the pump and the temperature of the bath gradually raised. When the vapour pressure of the substance contained in A becomes equal to the external pressure on the surface of the liquid in the tube, any further increase of temperature increases the pressure of the vapour in A which consequently bubbles

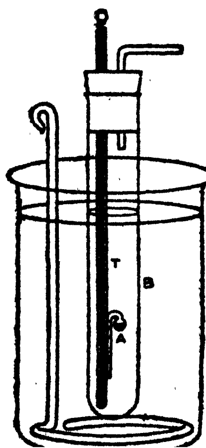


Fig. 7.—Smith and Menzies' Apparatus.

through the liquid in the tube. When this just happens the pressure recorded by the manometer gives the vapour pressure corresponding to the temperature indicated by the thermometer.

The boiling-point method has also been applied to metals by Braun. Zinc or cadmium was heated electrically in a quartz or porcelain tube and the temperature of the vapour was measured by a thermo-couple.

20. Discussion of Results.—Experiments show that the saturated vapour pressure of every substance increases as the temperature is raised. Hence the vapour pressure p must be a function of the temperature, viz., $p=f(T)$ where $f(T)$ must be of such form that its value increases with the temperature T. Various empirical relationships between p and T have been proposed from time to time. They hold for limited ranges and are by no means quite exact and universal.

In 1820 Young proposed a very simple formula

$$\log p = A + \frac{B}{T}, \qquad (5)$$

where T is the absolute temperature and A, B are constants. Kirchhoff in 1858 and Rankine in 1866 proposed quite independently the formula

$$\log p = A + \frac{B}{T} + C \log T. \qquad (6)$$

This formula agrees with experimental results very closely and can also be deduced from theoretical considerations. It is shown in Chapter X that

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}, \qquad (7)$$

where p is the vapour pressure, L the latent heat of vaporization, T the boiling point and v_2, v_1, the specific volumes of the substance in the liquid and vapour states. Neglecting v_1 in comparison with v_2 and replacing v_2 by RT/Mp from the gas laws we get

$$\log p = \frac{M}{R}\int \frac{LdT}{T^2} + i. \qquad (8)$$

Assuming L constant, equation (8) yields Young's formula (5). If, however, we assume L to vary linearly with temperature, *i.e.*

$$L = L_0 - \alpha T,$$

equation (8) yields us formula (6). In order to get the exact value of pressure corresponding to any temperature we must use an accurate expression giving the value of L as a function of T.

The above holds for the saturated vapour pressure of a pure liquid; when mixtures of two liquids are investigated they yield interesting results. (1) In case of liquids which do not at all mix the vapour pressure of the mixture is equal to the sum of the vapour pressure of the constituents, e.g., water and benzene or water and carbon disulphide.

(2) In case the liquids are partially miscible the vapour pressure is always less than the sum of the vapour pressures of the constituents and may even be less than that of one of them, *e.g.*, water and ether, or water and isobutyl alcohol. In this case each constituent dissolves a little of the other and the vapour pressure of the mixture remains constant over a large range of composition of the mixture but falls off for very dilute solutions finally attaining the limiting value for the pure constituent. Thus if we distil a weak solution of isobutyl alcohol, we find that the solution in the still becomes weaker and weaker till finally there is only pure water in the still and pure alcohol in the condenser. For a weak solution of water in alcohol the reverse is the case. (3) When the two liquids are wholly miscible, *e.g.*, water and methyl alcohol, the pressure is intermediate between those of the separate constituents. In this case whatever composition we start with, alcohol always passes to the condenser leaving pure water in the still.

21. Vapour Pressure over Curved Surfaces.—In the foregoing we have considered the vapour pressure over a flat surface. The vapour pressure over a curved surface is different on account of surface tension. Evaporation from a spherical drop produces a decrease in surface area and hence also in the surface energy due to surface tension and therefore, it will proceed further than in the case of a flat surface, *i.e.*, the vapour pressure over a convex surface will be greater than that over a flat surface. Detailed considerations yield the result

$$\log_e \frac{p_0}{p} = \frac{2S}{r} \cdot \frac{M}{\rho RT} \quad . \quad . \quad . \quad . \quad (9)$$

where p_0, p denote the vapour pressure over flat and curved surfaces respectively, S the surface tension, r the radius of curvature of the surface (considered positive for concave and negative for convex) and ρ the density of the liquid. These considerations have important consequences in the precipitation of rain and in the phenomenon of boiling. Equation (9) shows that if r is small and negative, *i.e.*, the surface is convex, p may become very large. Hence, if suitable nuclei for condensation are absent a high degree of supersaturation may be attained and inspite of it, no drops will be formed.

LATENT HEAT OF VAPORIZATION

22. In the measurement of latent heat of vaporization we have to remember two points ; first, that its absolute value is relatively high ; secondly, that the latent heat is absorbed or evolved in an isothermal change of state. The consequence is that its experimental determination is very little affected by the usual sources of error which are present in all calorimetric measurements. The methods can be grouped under three broad headings:

(A) *Condensation Methods.*—Those in which the amount of heat evolved when a certain amount of vapour condenses is measured.

(B) *Evaporation Methods.*—Those in which the amount of heat required to vaporize a given mass of the liquid is measured directly.

The heat is generally added in the form of electrical energy and can be easily determined.

(C) *Indirect Methods.*—Those in which the latent heat is calculated with the help of some thermodynamical relationship such as Clausius-Clapeyron relation (equation 7). From the vapour pressure curve the quantity dp/dT is determined and hence L evaluated from (7). We shall now consider the first two methods in greater detail.

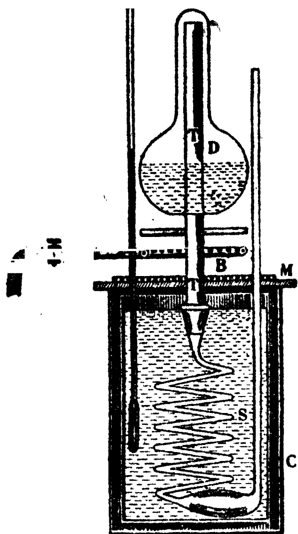


Fig. 8.—Berthelot's Latent Heat Apparatus.

A. Condensation Methods

23. Berthelot's Apparatus.—Regnault's experiments are rather of historical interest. We describe below the apparatus of Berthelot (Fig. 8). In this apparatus which is wholly of glass the liquid is kept in the vessel D and heated by the ring burner B. The rest of the apparatus is protected by an insulating mantle M. The evaporated gas passes through the tube T into the spiral S placed within the calorimeter C. The spiral S is fitted to T by a conical ground piece and can be easily removed. The vapour condenses within the spiral and gives off its latent heat of vaporization to the calorimeter which can be easily measured by observing the rise of temperature on the thermometer placed inside a water jacket. The amount of water condensed is obtained by weighing the spiral S before and after the experiment. The heat measured represents the heat of vaporization plus the heat given by the condensed liquid in cooling from the boiling point to the final temperature of the calorimeter. The open end of S is connected to a pump to regulate the pressure under which the boiling takes place.

Errors are likely to arise owing (1) to superheating of the liquid, (2) to minute drops of water being carried over by the vapour. As the use of a ring burner causes the heating to be sometimes irregular, Kahlenberg replaced the ring burner by a metallic spiral placed inside the liquid and heated electrically.

24. Awbery and Griffiths used a slightly modified apparatus in which the usual calorimeter was replaced by a continuous flow calorimeter. The apparatus is shown in Fig. 9. The boiling chamber is heated electrically by an inner coil. The vapour passes down the vertical tube which is surrounded by a jacket of water through which a stream of water flows at a constant rate. The temperatures of the inflowing and outflowing water are determined by two thermo-couples. There is a third thermo-couple at the mouth of the vertical tube which

gives the temperature of the condensed liquid as it leaves the apparatus. In this experiment the vapour must be produced at a steady rate and this is achieved by the use of electrical heating. The latent heat is obtained from the formula

$$M\theta = m[L + s(t_2 - t_1)]. \quad (10$$

where θ is the excess of temperature of the outflow water over the inflow water. M is the quantity of water flowing per unit time, m is the rate at which the liquid is being distilled, t_2 is the boiling point of the liquid, t_1 the temperature of the liquid as it leaves the apparatus.

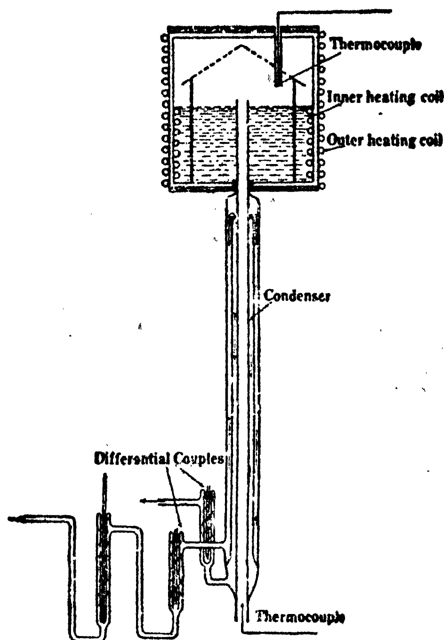


Fig. 9.—Awbery and Griffiths' Latent Heat Apparatus.

B. Evaporation Methods

25. This method was employed by Dieterici, who measured the heat required to evaporate a given mass of water with the help of a Bunsen ice-calorimeter. The water was contained in the tube A of the ice-calorimeter (Fig. 3, p. 34) and the heat was measured by finding the mass of mercury expelled. Griffiths found the electrical energy required to vaporize a given mass of water. We shall describe the apparatus used by Henning for precision measurement of the heat of vaporisation between 30° and 100°C.

26. Henning's Experiments.—The apparatus employed by Henning is indicated in Fig. 10. C is a copper vessel, one litre in capacity, in which the liquid is allowed to evaporate. This is surrounded by an oil-bath A maintained at a constant temperature. The heating takes place through the spiral D of constantan wire wound on a quadrilateral mica frame. E is a platinum resistance thermometer. The vapour which is evolved passes through the German silver tube H downwards through the German silver tube KK to the vessel P in which it is condensed and weighed. The end of H is bent downwards so that no liquid drops can be carried. The vapour is first led to one of the vessels P, and when the conditions become steady the stop-cock R is turned so that steam is led to the other vessel P. After a sufficient quantity of steam has been led to P the stop-cock R is turned to the other side.

The quantity of vapour deposited in the second vessel is now found by weighing and the quantity of heat supplied is obtained from observations of the electrical measuring apparatus. For determining the heat of evaporation at lower pressure, P is connected to a large vessel of about 5 litres capacity which is maintained by means of a water pump at the required pressure.

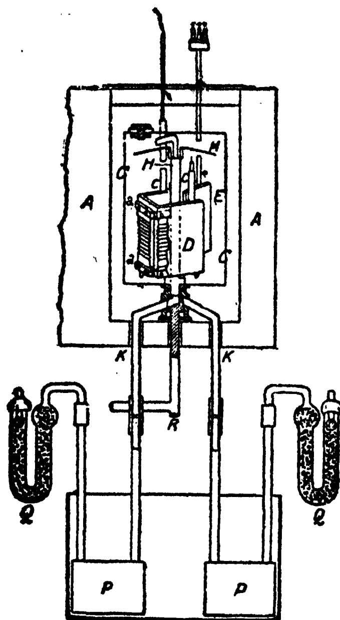


Fig. 10.—Henning's Latent Heat Apparatus.

A similar apparatus was employed by Henning for finding the heat of vaporization of water up to 180°C when the pressure reaches about 10 atmospheres. Fogler and Rodebush used this method for determining the latent heat of evaporation of mercury up to 200°C.

For determining the latent heat of evaporation of substances like nitrogen, hydrogen, helium, etc., which become liquid at very low temperatures, the above principle has been utilized by Dana and Onnes, Simon and Lange and others.

DISCUSSION OF LATENT HEAT DATA

27. Variation of the Latent Heat with Temperature.—Experiments show that the latent heat diminishes as the temperature at which boiling takes place is raised. This was noticed even by early investigators who proposed various empirical formulae. Of these Thiesen's formula appears to have been most satisfactory and states

$$L = L_1(t_c - t)^{\frac{1}{3}} \quad . \quad . \quad (11)$$

where t_c is the critical temperature and L_1 a constant which denotes the value of L at $t = t_c - 1$. This is of course based on the assumption that latent heat vanishes at the critical temperature. Henning showed that between 30° and 100°C the latent heat of vaporization of water is given by the formula

$$L = 538{\cdot}86 + 0{\cdot}5994(100 - t). \quad (12)$$

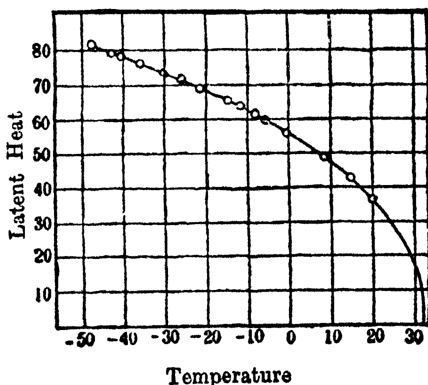


Fig. 11.—Variation of Latent Heat of CO_2 with temperature.

A typical curve showing the latent heat of carbon dioxide at various temperatures is given in Fig. 11. It is drawn from the results of several investigators and represents mean values. The figure shows clearly that the latent heat vanishes at the critical temperature of CO_2 which is about 31°C. This result is quite universal. The exact variation of latent heat with temperature for all substances is given by the thermodynamic formula

$$\frac{dL}{dT}-\frac{L}{T}=c_g-c_l-\frac{L}{v_2-v_1}\left\{\left(\frac{\partial v_2}{\partial T}\right)_p-\left(\frac{\partial v_1}{\partial T}\right)_p\right\} \quad . \quad . \quad (13)$$

where c_g, c_l 'enote the specific heat of the substance in the gaseous and liquid states respectively and v_2, v_1, the respective specific volumes.

28. Trouton's Rule.—As in the case of latent heat of fusion, we have here also an important generalization known as Trouton's Rule which states that *the ratio of the molar latent heat of vaporization to the boiling point is a constant for most substances;* or symbolically,

$$\frac{ML}{T_b}=\text{constant}. \quad . \quad . \quad . \quad . \quad (14)$$

where M is the molecular weight and T_b the boiling point. The value of the constant is about 21. The law does not hold for associated vapours. Table 3 shows that the law holds approximately for most substances.

Table 3.—Illustration of Trouton's Rule.

Substance	Gram-molecular latent heat in calories ML	Boiling point T_b	Value of $\frac{ML}{T_b}$ experimentally
Helium	22	4·29	5·1
Hydrogen	219	20·4	10·0
Nitrogen	1340	77·3	17·3
Oxygen	1630	90·1	18·1
Hydrochloric acid	3890	188·1	20·7
Chlorine	4600	239·5	19·2
Pentane	6100	309·0	19·75
Carbon disulphide	6490	319·2	21·0
Benzene	7350	353	20·8
Aniline	10000	457·0	21·9
Mercury	14200	630·0	22·6
Caesium	15600	858	18·2
Rubidium	18700	942	19·9
Sodium	23300	1155	20·2
Zinc	27730	1180	23·5
Lead	46000	1887	24·4

It will be seen, however, that ML/T is really not quite constant for all substances. A simple theoretical discussion shows that it cannot be so, for the boiling point under atmospheric pressure is purely an artificial point and has no physical significance. It varies enormously with the external pressure, while the latent heat varies neither in the same direction nor to the same extent. In the case of water the Trouton quotient at a few temperatures is given in Table 4.

Table 4.—Trouton quotient for water at different temperatures.

Pressure	B.P.	latent heat	Trouton quotient
4·6 mm.	0°C.	606·5 cal.	40
760 ,,	100°C.	535·9 ,,	25·9
20950 ,,	230°C.	446 ,,	16

From the variation in L and the boiling point it is evident that the Trouton quotient will go on decreasing as the temperature rises becoming zero at the critical temperature where the latent heat vanishes. Thus the quotient can have any value from 0 to 40 and it appears to be merely an accident that for most substances boiling under atmospheric pressure, the value is about 20.

DETERMINATION OF VAPOUR DENSITY

29. By vapour density we mean the specific gravity of the vapour referred to air or hydrogen as unity. The vapour density can be easily found if we find the volume occupied by a known weight of vapour at a certain pressure and temperature. Thus if w grams of the vapour occupy v c.c. at the pressure p and temperature T, and ρ_0 be the weight of 1 c.c. of the standard substance (air) at 273° and 760 mm. then the vapour density is given by

$$\frac{w}{\rho_0 v}\frac{T}{273}\frac{760}{p} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The density of the *unsaturated* vapour can be easily and accurately found by any one of the standard methods* *viz.*, of Victor Meyer, Dumas, Hofmann and others. But before 1860 there was no method for directly determining the density of *saturated vapours*. The methods adopted were all indirect in which the density of the unsaturated vapour was first determined, and assuming the perfect gas laws to hold up to the saturated state, the density of the saturated vapour was determined. This assumption is, however, not quite justifiable, hence these methods can never give accurately the density of saturated vapour. Still, however, they are frequently used especi-

* Full details of these methods will be found in any text-book on Physical Chemistry.

ally that of Victor Meyer, which is of considerable practical importance and is consequently described below.

The apparatus (Fig. 12) consists of a cylindrical bulb B with a long narrow stem, near the top of which there is a side-tube. The lower part of the tube is surrounded by a suitable temperature bath which is kept replenished by a suitable liquid boiling at some pressure in A. Air inside the tube gets heated and is expelled at the top; after a time, however, a steady state is attained when no more air escapes. The substance whose vapour density is to be determined is enclosed in a thin-walled stoppered bottle and placed inside the tube. By manipulating *s* it is allowed to drop gently in B. The bottle breaks, the liquid vaporizes and thereby displaces an equal volume of air which escapes at the side-tube and is collected in the tube *t*. Knowing the mass of this air, the density of the vapour of the substance is obtained by dividing the mass of the liquid taken by the mass of displaced air.

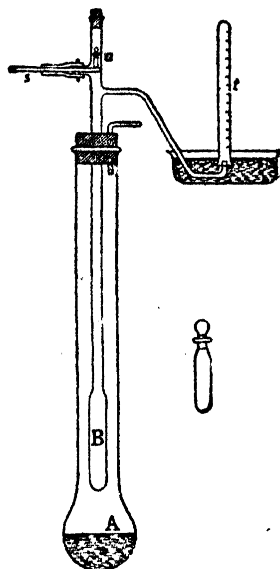


Fig. 12.—Victor Meyer's Vapour Density Apparatus.

Nernst has modified the apparatus and could thereby measure the vapour density of KCl and NaCl up to 2000°C while Wartenberg found the vapour density of several metals up to 2000°C. For a description see Arndt *Physikalish-chemische Technik*, Chap. IX.

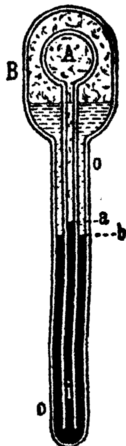


Fig. 13.—Fairbairn and Tate's apparatus.

30. Accurate determination of the Density of Saturated Vapour.—In 1860 Fairbairn and Tate devised an apparatus by means of which they measured the density of saturated vapour directly. Fig. 13 explains the principle of their apparatus. A is a spherical glass bulb whose narrow stem dips into mercury contained in the outer wider glass tube. The latter communicates with the metal reservoir B. Both A and B contain some water above the mercury levels, the latter containing a larger quantity than the former. All air is expelled from the apparatus and then both the vessels are surrounded by a bath whose temperature is gradually raised. The levels of the mercury in the two vessels remain constant, that in A being always higher than in B due to the excess of water in B. This is so as long as there is any liquid water in A. But as soon as the liquid in A disappears, the level of mercury in A suddenly rises. This is because the saturated vapour pressure increases much faster than the

pressure of unsaturated vapour obeying Boyle's law. The temperature at which this sudden rise of mercury column in A appears is noted. At this temperature the vessel A becomes filled with saturated vapour whose pressure may be found by means of a gauge connected to B. Knowing the mass of water in A and the volume of the enclosed space, the density of the vapour at the particular temperature and pressure can be calculated.

Somewhat later Perot attempted to isolate a portion of the saturated vapour and to weigh it. This could be very conveniently done by isolating the vapour by means of a stop-cock and getting it absorbed in dry calcium chloride and weighing the latter. K. Onnes employed another simple method. In a graduated vacuous tube different masses of the liquid are introduced and the volumes of the vapour and the liquid observed. Thus if m and m' grams of the substance are introduced and the volumes occupied by the gas and the liquid are v_1 and v_2 in the first case, and v_1', v_2' in the second case, and ρ_g, ρ_l represent the densities of the gas and the liquid, we have

$$m = v_1\rho_g + v_2\rho_l, \qquad m' = v_1'\rho_g + v_2'\rho_l,$$

whence

$$\rho_g = \frac{mv_2' - m'v_2}{v_1v_2' - v_1'v_2}. \qquad \qquad (16)$$

Book Recommended.

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, article on 'Latent Heat.'

CHAPTER VI

PRODUCTION OF LOW TEMPERATURES

1. Introduction.—In the early days of the study of Heat there seems to have been a widespread belief that nothing could be colder than ice. This point was, therefore, chosen in all earlier systems of temperature measurement as the zero (starting point) of the scale. But Fahrenheit showed that if the mercury thermometer was placed in a mixture of ice and common salt the thread of mercury went down much lower. Fahrenheit chose the lowest point reached in this way ($-18°C$) as his zero, but we now know that Fahrenheit's zero is not the lowest temperature obtainable. The study of the laws of perfect gases tells us that we can, at least theoretically, proceed on the centigrade scale 273 degrees below the melting point of ice and that this is the lowest temperature conceivable. This is taken as the zero of the absolute temperature scale. In this chapter we shall discuss the principles and contrivances by which the region from 0°C to absolute zero can be reached.

PRINCIPLES USED IN REFRIGERATION

2. For reaching low temperatures we have to utilize processes by which a body can be deprived of its total heat content. The following methods may be employed to achieve this end:—

(*i*) By adding a salt to ice.
(*ii*) By boiling a liquid under reduced pressure.
(*iii*) By the adiabatic expansion of a gas doing external work.
(*iv*) By utilizing the cooling due to Joule-Thomson effect.
(*v*) By utilizing the cooling due to Peltier effect.
(*vi*) By utilizing the heat of adsorption.
(*vii*) By the process of adiabatic demagnetisation.

A general theory of refrigeration will be given later in Chap. IX; here we shall simply discuss the principles and contrivances for utilizing them.

(*i*) Adding a Salt to Ice

3. Low temperatures may be attained by *adding a salt to ice*. This is the same process which was employed by Fahrenheit. The cause of this lowering of temperature is easily understood. Pieces of ice have generally some water adhering to them, and if salt be added to this ice, it is dissolved by the water and more ice melts. The necessary heat for this process, *viz.*, the heat of solution and the latent heat required to melt the ice, is extracted from the mixture itself whose temperature consequently falls down.

This is the principle of *freezing mixtures*. This process, however, cannot go on indefinitely. Fig. 1 shows the freezing curves obtained with ammonium chloride, the ordinate representing temperature in °C and abscissa the concentration of the salt. When the salt is added to ice the temperature of the mixture changes as represented by the line AB till the *eutectic temperature* of −15·8°C is reached. Temperatures lower than this cannot be obtained in this way for when more salt is added it no longer goes into solution. The curve AB represents equilibrium between solution and ice while CB represents equilibrium between salt and solution and B denotes the *eutectic mixture* with a fixed composition and fixed temperature.

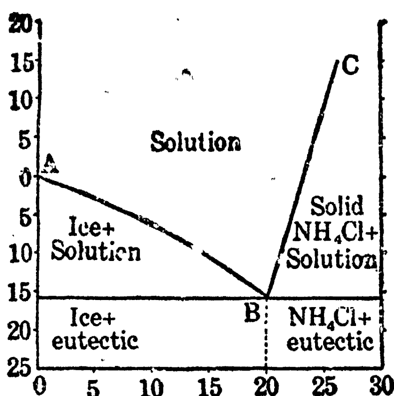


Fig. 1.—NH_4Cl and water system.

In Table 1 the composition of the eutectic mixture and the corresponding eutectic or cryohydric temperatures are given for a number of commoner salts. Generally hydrated salts are employed and in that case the corresponding quantity of the hydrated salt should be obtained by calculation. These eutectic temperatures represent the lowest temperature that is possible to attain with that freezing mixture.

Table 1.—Freezing Mixtures.

Salt	Anhydrous salt per 100 grams of the mixture.	Eutectic temperature.
$MgSO_4$	19·7	—3·9°C
$ZnSO_4$	27·2	—6·5
KCl	19·7	—11·1
NH_4Cl	18·6	—15·8
NH_4NO_3	41·2	—17·4
$NaNO_3$	37	—18·5
NaCl	22·4	—21·2
$MgCl_2$	21·6	—33·6
$CaCl_2$	29·8	—55
KOH	31·5	—65

(*ii*) Boiling a Liquid Under Reduced Pressure

4. Low temperature may also be attained by allowing a liquid to boil under reduced pressure. When a liquid evaporates it requires heat for conversion from the liquid to the gaseous state (latent heat of vaporization). Thus one gram of water at 100°C requires 539 calories for complete evaporation. If such liquid be forced by some contrivance to evaporate rapidly and if the liquid be isolated, this is supplied at the expense of its total heat content and intense cooling may be produced.

The oldest contrivance for utilising this process is the cryophorus indicated in Fig. 2. The bulb B contains water or some more volatile liquid and the rest of the space is filled with the vapour of

the same liquid. When A is immersed in ice the vapour in it condenses and the pressure of the vapour in B becomes so much lowered that the liquid in B boils. The latent heat necessary for this purpose is extracted from the rest of the liquid which consequently freezes.

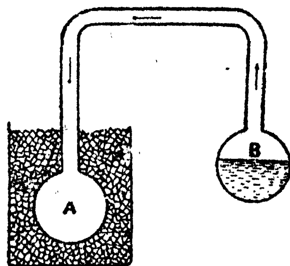


Fig. 2.—The Cryophorus.

Now-a-days this principle is employed in a large number of refrigerating machines both for industrial and domestic work. Water, however, is not a suitable liquid to use for though it has a large latent heat of evaporation, the vapour pressure at low temperatures is small. The liquids commonly employed are ammonia, sulphur dioxide, etc. Two types of such machines are in use:—(1) Vapour compression machines, (2) Vapour absorption machines. The vapour compression machines are more efficient, particularly for large plants, and require less initial cost; consequently, their use is more common than that of the other. The only essential difference between these two types of machines consists in the manner of compressing the low pressure vapour. In the former a motor compressor is used while in the latter a dilute aqueous solution at ordinary temperatures is employed to dissolve the low pressure vapour and the concentrated solution is heated in a generator to expel the gas at high pressure. We shall now describe these machines in greater detail.

5. Vapour Compression Machine.—Fig. 3 shows the essential parts of a vapour compression machine. There are three prin-

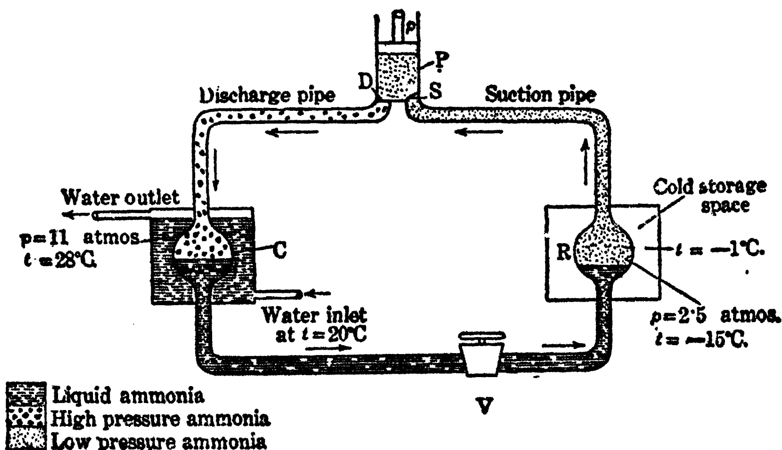


Fig. 3.—Essential parts of a Vapour Compression Machine.

cipal parts—the compressor P, the condenser C and the refrigerator or evaporator R. The cylinder of the compressor has two valves,

S and D, the former for the suction of the low pressure vapour from the evaporator and the latter for the discharge of the compressed vapour to the condenser. When the piston p moves upwards the pressure in the cylinder falls below the pressure in the evaporator and hence the low pressure vapour is sucked in through S and the suction pipe. During the downward stroke the vapour is compressed and then delivered to the condenser C through the discharge valve D and the discharge pipe. The condenser is cooled by cold water circulating in the outer chamber. On account of the low temperature and high pressure the vapour liquefies in C. This liquid passes through the expansion valve or the regulating valve V which is simply a throttling valve to reduce the pressure of the liquid from the high pressure prevailing in the condenser to the low pressure in the evaporator. Due to the low pressure the liquid boils thereby extracting its latent heat from the cold storage space surrounding the evaporator. This space is consequently cooled. In some cases the evaporator is surrounded by brine water kept in circulation. The brine water thus becomes cooled and is taken elsewhere for refrigerating purposes. The low pressure vapour is sucked in by the compressor and the cycle of operations continues.

In the diagram anhydrous ammonia is supposed to be utilised as the refrigerant. The pressures and temperatures of ammonia in different parts of the apparatus are approximately as indicated in the figure.

A complete vapour compression machine is shown in Fig. 4 which, however, utilises sulphur dioxide as the refrigerant. Vapour compression machines are now extensively employed in ice-making, in preserving meat and other foodstuffs and for various other industrial purposes.

6. Refrigerants.—Various liquids have been used as refrigerants, the important ones being ammonia, sulphur dioxide, ethyl chloride and methyl chloride. Of these ammonia is most commonly used in large refrigerating plants, while sulphur dioxide is employed in many household plants. There are various criteria for selecting a suitable refrigerant: (1) The latent heat of the refrigerant should be large so that the minimum amount of liquid may produce the desired refrigerating effect. (2) The refrigerant must be a vapour at ordinary temperatures and pressures but should be easily liquefied when compressed and cooled. Generally a temperature of about 5°F (somewhat below ice-point) is required in the evaporator coils and about 86°F (about room temperature) in the condenser coils. (3) The pressure of the vapour of the refrigerant in the evaporator coil must be greater than the atmospheric pressure so that atmospheric impurities may not be sucked inside and later block the valves. With cooling water at room temperature surrounding the condenser the pressure necessary to liquefy the gas in the condenser should not be too large otherwise the compressor and the cylinder will have to be made very stout and consequently costly and there will be much leakage of the vapour into the atmosphere. (4) The specific volume of the vapour

of the refrigerant should not be large otherwise a very large compressor will be necessary.

The important properties of some common refrigerants are given in Table 2. From this table it is evident that ammonia is the most suitable refrigerant. One pound of ammonia will produce the same amount of refrigeration as 8·75 pounds of carbon dioxide while the pressure in the condenser in case of carbon dioxide is about 6 times greater than in the case of ammonia. In the matter of specific volume, however, carbon dioxide possesses an advantage. Sulphur dioxide requires a less stout compressor and condenser than ammonia but for the same refrigerating effect the compressor has to be made large.

*Table 2.—Characteristics of refrigerants**

	Ammonia	Sulphur dioxide	Carbon dioxide	Methyl chloride	Freon CCl_2F_2
1. Boiling point in °F at atm. pressure ..	—28·0	14·0	—108·4	—10·6	—21·7
2. Latent heat of evaporation at 5 °F in B.t.u. per pound ..	565·0	175·6	114·7	178·5	69·5
3. Refrigerating effect in B.t.u. per lb. ..	474·45	141·37	56·69	148·7	51·07
4. Vapour pressure at 5°F in lb/in².	34·27	11·81	334·4	20·89	26·51
5. Vapour pressure at 86°F in lb/in²	169·2	66·45	1039·0	95·53	107·9
6. Specific volume of vapour in evaporator in cu. ft. per lb.	8·150	6·421	0·267	4·529	1·48
7. Horse-power for a refrigerating effect of 200 B.t.u. per min.	0·99	0·99	1·87	1·06	0·997

* A number of new refrigerants have been introduced during the last twenty years. Among these are Freon or dichlorodifluoromethane (CCl_2F_2), Carrene (CH_2Cl_2), trichloro-monofluoro-methane ($CFCl_3$), dichloro-tetrafluoro-ethane ($C_2Cl_2F_4$) etc. Of these Freon is the one most commonly used. For an account of the properties of these refrigerants see *Refrigerating Data Book* (1943-44) published by American Society of Refrigerating Engineers, New York.

This method may be employed to obtain extremely low temperatures by using liquid hydrogen and helium. These liquids are allowed to boil under reduced pressure when temperatures lower than their normal boiling points are reached.

7. Electric Refrigerator.—Fig. 4 shows a modern electric refrigerator known as the Frigidaire, working automatically on the vapour compression principle. Here liquid sulphur dioxide is used as the refrigerant. The part above the dotted line is the cold storage space.

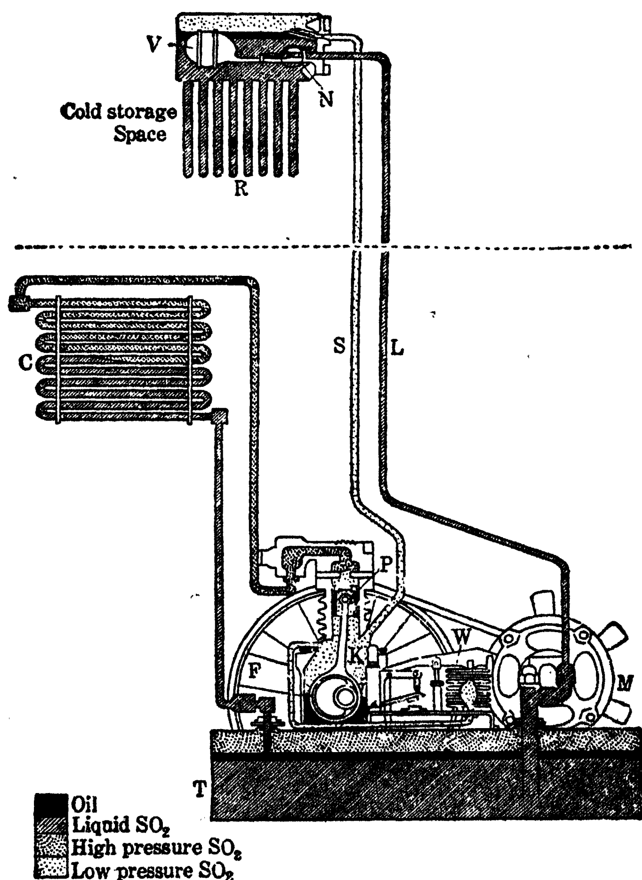


Fig. 4.—Frigidaire.

The refrigerator coil R contains liquid sulphur dioxide which extracts heat from the surrounding space and evaporates and the low pressure vapour collects at the top. This vapour communicates with the suction pipe S and the crank case K to the motor switch W. When enough gas has collected in the top of R it exerts a large pressure which is transmitted through S and K thereby operating the switch

W. This starts the motor and the latter works the compressor P, as a result of which, the low pressure vapour is sucked in through S to the crank case and compressed by the piston and delivered to the condenser C. The condenser is cooled by a current of air forced across it by the fan mounted on the motor M but in some cases the cooling is brought about by the flywheel itself whose spokes are shaped like the blades of a fan. The high pressure sulphur dioxide vapour on being thus cooled liquefies and collects in the reservoir T. From here on account of the high pressure the liquid is forced up through the liquid pipe L and enters R through the needle-valve N. When enough liquid has collected in R the float valve V rises and closes the needle valve N. Thus the machine works only when the gas pressure in R becomes large and liquid is transferred from the storage tank T to R only when the quantity of liquid in R becomes less and the float valve has sunk so as to open the needle valve N.

8. Ammonia Absorption Machine.—As already stated the absorption machines differ from the vapour compression machines only in the manner of converting the low pressure vapour into high pressure vapour. Amonia is the most suitable refrigerant for use in absorption machines, and water is a very suitable absorber. Water at 55°F absorbs about one thousand times its volume of ammonia vapour but when the aqua ammonia solution is heated to 80°F ammonia vapour freely escapes from the solution.

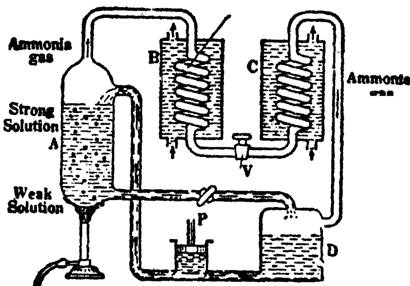


Fig. 5.—Ammonia Absorption Machine.

The working of an ammonia absorption machine will be easily understood from Fig. 5. The generator A contains a strong solution of ammonia gas in water and is heated by a burner as shown in the figure or by means of pipes carrying steam. Ammonia gas is expelled from the solution and passes into the coils immersed in the condenser B through which cold water continuously flows. The gas condenses there under its own pressure into liquid ammonia. The liquid ammonia thus formed passes through a narrow regulating valve V to the spiral immersed in the refrigerator C, where on account of the low pressure it evaporates. The valve is adjusted to maintain the desired difference of pressure on the two sides. Through the refrigerator flows a stream of brine water which becomes cooled by the evaporation of ammonia. The cool brine solution may be taken to any place for refrigerating purposes.

The ammonia gas formed in the coils in C is absorbed by water or dilute ammonia solution contained in the absorber D and thus the pressure is kept low. The solution in D becomes concentrated and is transferred by the pump P to the generator at the top. Thus

the supply of concentrated ammonia solution is kept up. Dilute ammonia from the bottom of the generator may be run to the absorber and concentrated. Thus the cycle is repeated and the action is quite continuous.

The difficulties of this machine are that it has a low efficiency and the pressures are widely different in the condenser and the evaporator. The low efficiency is due to the circumstance that the heat absorbed by the ammonia in the generator is much larger than the heat absorbed by it in the evaporator coils. Further the machine has a moving part in the pump needed to transfer the liquid to the generator, and is costly. All these difficulties are avoided in a clever invention by two Swedish engineers, von Platen and Munters, which is placed in the market under the name Electrolux Refrigerator. In this Dalton's law of partial pressures is used to make the total pressure in the condenser and the evaporator equal, maintaining at the same time a difference in partial pressures of ammonia in the two chambers ; this is accomplished by using an inert gas like hydrogen at a pressure of 9 atmos., the partial pressure of ammonia being 3 atmos. in the evaporator and the absorber, and ammonia liquefies in the condenser at the pressure of 12 atmos. Concentrated ammonia solution is forced up into the generator by heat and not by a pump.

(*iii*) Adiabatic Expansion of Compressed Gases

9. Cooling produced by the sudden adiabatic Expansion of compressed gases. —If a highly compressed gas be suddenly allowed to expand adiabatically, it cools very considerably on account of the large external work it does in expanding, vide §23, Chap. II where it is shown that $T' = T(p'/p)^{(\gamma-1)/\gamma}$. The cooling may be so great that the gas may even solidify.

An example which is easily available in a big town is afforded by cylinders containing carbon dioxide. If such a cylinder be suddenly opened and a piece of cloth held before it, the issuing gas is deposited in the form of solid CO_2 (called dry ice commercially).

This priciple was utilised by Cailletet who first liquefied oxygen in 1877. He compressed oxygen to a pressure of 300 atmospheres in a strong capillary tube cooled to $-29°$C by liquid sulphur dioxide boiling under reduced pressure and then suddenly released the pressure. A mist of liquid oxygen was formed which disappeared in a few seconds. Pictet compressed oxygen to a pressure of 500 atm. and cooled it to about $-130°$C by liquid carbon dioxide evaporating under reduced pressure. Then he suddenly released the pressure. Oxygen in the form of a white solid was thereby obtained. In 1884 Wroblewski obtained a mist of hydrogen while in 1893 Olszewski obtained liquid hydrogen in sufficient quantities, by cooling compressed hydrogen with liquid oxygen and then suddenly releasing the pressure. Simon in 1933 produced appreciable quantities of liquid helium by sudden adiabatic expansion of the compressed gas which had been precooled by solid hydrogen evaporating at reduced pressure.

The process is, however, essentially discontinuous, hence for commercial purposes it was almost discarded ; but a novel way of utilizing the principle has been invented by Claude and Heylandt for liquefying air (see sec. 22).

We have described above two types of refrigerating machines. There is a third type also which is sometimes employed. This may be called the air compression machine because air is here used as the refrigerant. In this air is first compressed in a compressor, the heat of compression is then removed by passing the gas through coils kept cool by cold circulating water. This cool compressed air then suffers adiabatic expansion in the expansion cylinder and becomes considerably cooled. This cold air then traverses the cold storage space and thus gets heated and is again compressed. Thus the cycle continues. This is the principle of the Bell-Coleman refrigerator largely used for the refrigeration of cold storage chambers in ships.

(*iv*) Cooling due to Peltier Effect

10. It is well known that when an electric current flows in a circuit from bismuth to antimony through a junction, this junction is cooled. This is known as the Peltier effect and may be utilized in producing cooling. This cooling is rather small though semi-conductor thermo-junctions have recently produced much more cooling, and have been employed in some refrigerators.

(*v*) Cooling by Joule-Thomson Expansion

11. This method is of considerable importance and will be considered in detail later in this chapter.

(*vi*) Cooling Due to Desorption

12. Charcoal adsorbs a number of gases which are released on lowering the pressure, and when these gases escape, a cooling results in a manner somewhat analogous to the case of evaporation of liquids. This is called the "Desorption method" and was utilised by Simon. In an experiment charcoal adsorbed helium gas at 5 atm. and 10°K and subsequent desorption to 0·1 mm. pressure lowered the temperature to 4°K which is sufficient to liquefy helium.

LIQUEFACTION OF GASES

13. Liquefaction by application of pressure and low temperature. —Substances, which are gaseous at ordinary temperatures may be converted to the liquid state if they are sufficiently cooled, and simultaneously a large pressure be applied to the mass. When pressure is applied the molecules come closer together and if heat motion be sufficiently small, they may coalesce, and form a liquid mass. If the liquid so cooled be allowed further to evaporate rapidly, still lower temperatures may be obtained. The production of extremely low temperatures is thus intimately connected with the problem of liquefaction of such gases which ordinarily show themselves to be very refractory.

The earliest scientist to try this effect of combined cooling and compression was Faraday* who, as early as 1823, employed the apparatus shown in Fig. 6 for liquefying chlorine. One end of the bent glass tube contains the substance from which chlorine is liberated by heat while the other end is immersed in a freezing mixture. Gaseous chlorine collects in the other end and finally liquefies under its own pressure. By applying this process Faraday and others succeeded in liquefying a large number of gases but some *viz.*, oxygen, nitrogen, hydrogen, carbon monoxide and methane baffled all attempts at liquefaction, though sometimes enormous pressures up to 3000 atm. were used. They were, therefore, termed *permanent* gases.

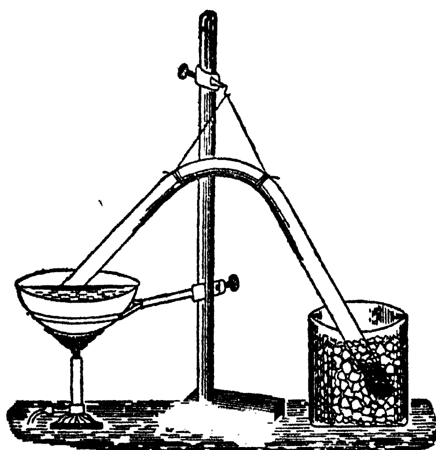


Fig. 6.—Faraday's Apparatus for Liquefaction of Chlorine.

Discovery of the Critical Point.—The causes of these failures became apparent with Andrews' discovery of the critical temperature in 1863. This subject has already been treated in Chapter IV. Andrews' experiments first clearly showed the importance of the critical phenomena. They established clearly that for every substance, which usually occurs in the gaseous form, there exists a temperature above which it cannot be liquefied however high may be the pressure to which it is subjected. Hence, in order to liquefy a gas by this method it must be pre-cooled below its critical temperature.

The determination of the critical point (p. 100) is not, however, easy. The early workers did not in fact, wait for its determination. They cooled the gases by ordinary methods as much as they could, and then applied high pressures.

14. The principal methods of liquefying air and other gases are the following :—(1) Pictet's cascade method which utilises a series of liquids with successively lower boiling points but the principle is the same as explained above; (2) the Linde and Hampson's methods employing the Joule-Thomson effect; (3) the Claude and Heylandt methods which utilise the cooling produced when a gas expands doing

* Michael Faraday (1791-1867), the "prince of experimenters," was born of humble parents in London. At the age of thirteen he became errand boy to a bookseller but later on in 1813 he got employment under Sir Humphrey Davy at the Royal Institution where he carried on his scientific work and finally succeeded Davy in 1827 as Director of the Royal Institution. His greatest work is the discovery of electromagnetic induction in 1831.

external work. We shall now consider these methods in greater detail. Of these the first is historically the oldest and theoretically the most efficient but is somewhat cumbersome and is very little used at present.

15. The Principle of Cascades or Series Refrigeration.—The method was first employed by R. Pictet in 1878. In principle it may be described as a number of compression machines in series. Pictet employed machines containing sulphur dioxide and carbon dioxide and obtained temporarily a jet of liquid oxygen by allowing compressed oxygen to expand adiabatically. Wroblewski and Olszewski at Cracow obtained sufficient quantities of liquid oxygen, nitrogen and carbon monoxide by the cascade method and determined their properties. Olszewski used ethylene as another intermediary below carbon dioxide and could thereby cool these gases below their critical temperature. Kamerlingh Onnes later employed the combination of methyl chloride and ethylene for liquefying oxygen. The principle of the method is illustrated in Fig. 7. Machine (1) utilizes methyl chloride. This has got a critical temperature of 143°C and hence at room temperature it can be easily liquefied by the pressure of a few atmospheres only. Water at room temperature flows in the

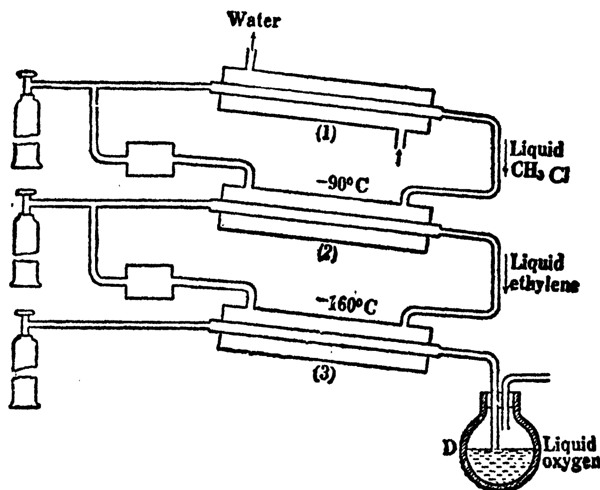


Fig. 7.—Illustration of the Method of Cascades.

jacket in (1). Liquid CH_3Cl falls into the jacket in (2) which is connected to the suction side of the compression pump. Thus the liquid evaporates under reduced pressure and its temperature falls to about −90°C. The compressor returns compressed CH_3Cl gas through the tube inside jacket (1), which is shown straight but is really in the form of spirals.

Inside the jacket (2) is placed the condenser coil through which ethylene passes from the compressor or the gas cylinder. It liquefies and then enters the jacket (3). There it evaporates under reduced

pressure and lowers the temperature to about −160°C. Through the tube inside jacket (3) oxygen from a cylinder passes and liquefies under pressure. Liquid oxygen is collected in the Dewar flask D. The lowest temperature obtained by boiling oxygen under reduced pressure is −218°C which is higher than the critical temperatures of neon (−228·7), hydrogen (−240°C) and helium, hence the method of cascades failed to liquefy these three gases.

The method of cascades is very useful for laboratory purposes. The use of the compressor can be entirely dispensed with by the use of suitable liquids boiling under atmospheric or reduced pressure. The suitable liquids can be selected from Table 3 which gives the normal boiling point, the critical temperature and the triple point for the common gases. The interval between the critical temperature and the triple point represents the range in which the liquid is available. Still lower temperatures can be obtained by further reducing the pressure over the liquid when it solidifies. Thus, using solid nitrogen and a good pump a temperature of about −224°C can be obtained which is still above the critical temperature of neon and it is not possible to bridge the gaps between nitrogen and neon and between hydrogen and helium in this way.

Table 3.—Critical temperature, normal boiling point and triple point of gases

Substance	B. P. at 1 atm. pressure	Critical temperature	Triple point
Methyl chloride	−24·09°C	143·3°C	−102·9°C
Sulphur dioxide	−10·1	157	...
Ammonia	−33·35	131·9	−77·7
Carbon dioxide	−78·6	31·0	−56·6
Nitric oxide	−89·8	36·50	−102·3
Ethylene	−103·72	+9·50	−169
Methane	−161·37	−82·85	−183·15
Carbon monoxide	−190·0	−138·7	...
Oxygen	−182·95	−118·82	−218·4
Nitrogen	−195·78	−147·13	−209·86
Neon	−245·92	−228·71	−248·67
Hydrogen	−252·76	−239·91	−259·14
Helium	−268·83	−267·84	...

16. Production of Low Temperatures by utilizing the Joule-Thomson Effect.—As the above method is not capable of liquefying hydrogen and helium, another process began to be utilized from 1898. This is the Joule-Thomson effect discovered in 1852. A full mathe-

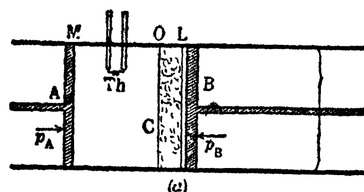
matical analysis of the phenomenon is postponed to Chapter X. We shall describe the phenomenon here.

We have already decribed Joule's experiment (p. 47) which showed that for permanent gases the internal energy does not depend upon volume, i.e., $\left(\frac{\partial u}{\partial v}\right)_T = 0$. This is called Joule's law or Mayer's hypothesis and is the characteristic property of a perfect gas (for perfect monatomic gases $U = \frac{3}{2}NkT$ per mol.). But this is not strictly true for the actual gases of nature ; they all show deviations from the state of perfectness and hence for them U is not independent of volume. A slight change in the temperature of the gas should occur in Joule's experiment, but since the capacity for heat of the contained air is negligible as compared to the heat capacity of the surrounding water, no change in temperature could be observed. In 1852 Lord Kelvin, in collaboration with Joule, devised a modification of Joule's experiment in which very small changes in temperature produced by expansion could be easily measured. This is called the "Porous plug" experiment and provides an unfailing test of Mayer's hypothesis. With its help we can easily find how far a gas deviates from the state of being perfect. Before proceeding to describe this experiment we shall discuss the theory underlying it.

17. Elementary Theory of the Porous Plug Experiment.—In this experiment a highly compressed gas is being continuously forced at a constant pressure through a constricted nozzle or porous plug. The plug, as its name implies, consists simply of a porous material, say, cotton-wool, silk, etc. having a number of fine holes or pores and is thus equivalent to a number of narrow orifices in parallel. The gas during its passage through the pores becomes throttled or wire-drawn, *viz.*, molecules of the gas are drawn further apart from one another doing *internal work* against molecular attractions. This is always the case whenever a fluid has to escape through a partly obstructed passage. On either side of the plug constant pressures are maintained, the pressure on the side from which the gas flows being much greater than on the other side since the plug offers great resistance to the flow of the gas. This expansion is of a character essentially different from Joule's expansion. In Joule expansion, the gas expanded without doing any external work. Here it expands against a constant external pressure and hence it has to do *external work* also, together with any internal work, while some work is done on the gas as well. The plug is surrounded by a non-conducting jacket so that the process is adiabatic in the sense that no heat enters or leaves the system. For such processes we now proceed to show that the total heat function $h = u + pv$ remains constant.

To prove this theorem, let us consider a mass of the fluid traversing the porous plug C from left to right as indicated in Fig. 8. Let p_A, v_A, T_A, u_A and p_B, v_B, T_B, u_B be the pressure, volume, temperature and internal energy of one gram of the fluid before and after traversing the orifice respectively. Suppose that one gram of

the gas is contained between the porous plug and some point M on the left and also between the plug and some point N on the right. For visualising the process we may assume an imaginary piston A at M separating this quantity of the gas, and that the flow of the gas is caused by the forward motion of the piston A. Actually, however, the rest of the gas exerts a pressure p_A at M which is maintained by the source of supply. The gas after traversing the plug pushes forward the imaginary piston B whose motion is opposed by the pressure p_B of the gas to the right of B. The initial and final states are shown respectively at (a) and (b) in the figure, the initial volume of the gas being equal to ML and the final volume equal to ON.



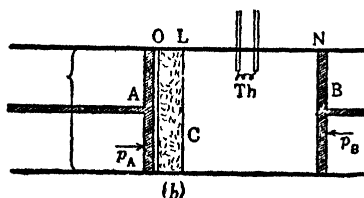


Fig. 8.—The Porous Plug Experiment.

The gas during its passage through the orifices in the plug has to overcome friction, viscosity, etc., and hence loses energy. The escaping gas issues in the form of eddies and its temperature falls considerably just at the jet (and this effect is spurious) because some thermal energy is now converted to the energy of mass motion. The eddies, however, subside after traversing a short distance and the temperature consequently rises. Let us consider only the steady flow before and after transmission through the orifice, *i.e.*, at points far removed from the plug where eddies are not present. We assume that the gas moves very slowly so that the energy of mass motion is very small and negligible in comparison to the energy of thermal motions. Now our initial system is ML and the final system is ON. But the plug OL is initially and finally in the same state ; hence the change simply consists in a change from MO to LN. If in addition, the tube is surrounded by a non-conducting material, no heat is supplied to or withdrawn from the system. Some work is, however, done by the external forces on the slowly moving system The force acting at A is equal to $p_A \times S$ where S is the cross-sectional area of the cylinder. The work done by this force upon the gas is $p_A \times S \times \text{MO} = p_A v_A$. Similarly, the work done by the gas in forcing the piston B is $p_B v_B$. Therefore, the net work done by the gas is $p_B v_B - p_A v_A$, and from the first law of thermodynamics, since $\triangle Q = 0$, the work done by the system is equal to the decrease in its internal energy, viz.,

$$u_A - u_B = p_B v_B - p_A v_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$u_A + p_A v_A = u_B + p_B v_B \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence $u + pv$ remains constant in the throttling process.

For perfect gases Boyle's law $(pv)_T =$ constant and Joule's law $u = cT$ hold true, and therefore $u+pv$ would depend upon temperature only. We have just shown that $u+pv$ for the porous plug experiment is constant whether the gas is perfect or not. Hence, for perfect gases the temperature on both sides of the plug would remain the same. In actual experiments, however, a cooling effect was observed for most gases such as air, O_2, N_2, CO_2 and a heating effect in case of H_2. Thus none of the gases examined was perfect. The lack of perfectness may be due either to deviations from Boyle's law or from Joule's law or both. If we know the former, as from Amagat's experiments (p. 97) we can find the latter by performing the porous plug experiment. If at the particular pressure and temperature in A, the gas is more compressible than at lower pressures [*cf.*, curves of N_2, CO_2 before the bend (p. 98)]. $p_A v_A < p_B v_B$. Therefore, due to deviations from Boyle's law alone $u_B < u_A$, *i.e.* the gas would show a cooling effect.* If the gas is less compressible (*cf.*, H_2) there would be a heating effect. Upon these effects will be superposed, the effect due to deviation from Joule's law. Since in actual gases, cohesive forces are present, work will be done in drawing the molecules further apart during expansion and the gas would become cooled. Thus the Joule-Thomson effect due to this cause would always be a cooling effect. The observed effect is the resultant of these two effects and may be a heating or cooling effect depending upon the sign and magnitude of the former effect.

18. The Porous Plug Experiment.— We shall now describe an actual experiment. Joule† and Thomson were the first to carry out these experiments. They employed a cylindrical plug, which is indicated in Fig. 9. The compressed gas flows through a copper spiral immersed in a thermostat and after having acquired its temperature, passes through the porous plug W. The plug consists of silk, or cotton-wool or other porous material, kept in position between two pieces of wire-gauze and enclosed in a cylinder of some non-conducting wood *bb*. The plug and part of the tube is surrounded by asbestos contained in a tin cylinder *zz* so that no heat reaches it from the bath. Joule and Thomson worked with air, O_2, N_2, CO_2 between 4° and 100°C, the initial and final pressures being 4·5 atmospheres and 1 atmosphere respectively.

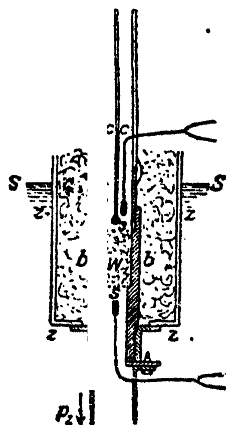


Fig. 9.—Joule-Thomson's porous plug.

* It is important to remember that the internal energy is made up of two parts : (1) kinetic energy which depends upon the temperature, (2) potential energy due to molecular attractions, the former being much greater in a gas under ordinary conditions so that Joule's law is approximately obeyed.

† Joule, *Scientific Papers*, Vol. II. p. 216.

Some of the subsequent workers employed a plug of the "axial flow" type as used by Joule and Thomson, while some others employed a plug of the "radial flow" type. In the latter the gas flowed from the outer side of a hollow cylindrical plug to the interior and hence heat-insulation was better. Certain others employed only a throttle valve or a restricted orifice.

From these experiments Joule and Thomson found that the fall in temperature was proportional to the difference in pressure on the two sides of the plug, *i.e.*, $\delta\theta = k(p_A - p_B)$, where k is a constant, characteristic of the fluid. They found empirically that $k = A/T^2$ where T is the absolute temperature of the gas, while Ross-Innes found $k = A + B/T$. Hoxton, however, found that his results were best represented by the formula

$$k = A + \frac{B}{T} + \frac{Cp}{T^2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We can find a value of k from theoretical considerations (see Chap. X). If the gas be supposed to obey van der Waals' equation of state, it can be shown that the Joule-Thomson effect

$$\frac{\Delta\theta}{\Delta p} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \text{ approx.} \quad . \quad . \quad (4)$$

Exercise 1.—Using the values of $a = 1{\cdot}36 \times 10^6$ atm. cm⁴ and $b = 32{\cdot}0$ c.c. for a gram-molecule of oxygen at N.T.P. and $C_p = 7{\cdot}03$ cal. per mol., calculate the Joule-Thomson effect from equation (4).

$$\frac{\Delta\theta}{\Delta p} = \frac{1}{7{\cdot}03 \times 4{\cdot}18 \times 10^7}\left[\frac{2 \times 1{\cdot}36 \times 10^6 \times 1{\cdot}01 \times 10^6}{8{\cdot}3 \times 10^7 \times 273} - 32{\cdot}0\right]$$

or
$$\frac{\Delta\theta}{\Delta p} = \frac{89}{7{\cdot}03 \times 4{\cdot}18 \times 10^7}\frac{\text{deg.}}{\text{dyne/cm}^2}$$

$$= \frac{89 \times 1{\cdot}01 \times 10^6}{7{\cdot}03 \times 4{\cdot}18 \times 10^7} = 0{\cdot}31\ \frac{\text{deg.}}{\text{atm./cm}^2}.$$

Exercise 2. Calculate for a van der Waals' gas the cooling produced in the Joule-Thomson process.

Internal work done by the gas $= \int_{V_1}^{V_2} \frac{a}{V^2}\,dV = \frac{a}{V_1} - \frac{a}{V_2}$.

Net work (external + internal) done by the gas

$$= p_2V_2 - p_1V_1 + \frac{a}{V_1} - \frac{a}{V_2}$$

$$= R(T_2 - T_1) + b(p_2 - p_1) + \frac{2a}{V_1} - \frac{2a}{V_2},$$

since from van der Waals' equation $pV = RT + bp - (a/V)$ approx. for the two sides of the plug.

This will produce a cooling by $-\Delta\theta$ (since $\Delta Q = 0$) such that (see Chap. X, sec. 10)

$$-C_v\Delta\theta = R(T_2 - T_1) + b(p_2 - p_1) + \frac{2a}{V_1} - \frac{2a}{V_2}$$

or $$-C_v \triangle\theta = R\triangle\theta + b\triangle p + \frac{2a}{RT}(-\triangle p) \text{ approx.}$$

Combining this with the relation $C_p - C_v = R$, we get equation (4).

19. Principle of Regenerative Cooling.—The Joule-Thomson cooling observed for most gases is very small. Thus, for air at a temperature of 20°C when the pressures on the two sides are 50 atmospheres and 1 atmosphere respectively, Joule and Thomson found that the temperature falls by 11·7°C. Hence the method could not be employed for a long time for producing liquefaction. Subsequently, however, it was discovered that the cooling effect can be intensified by employing what is called the *regenerative* process. A portion of the gas which first suffers Joule-Thomson expansion and becomes cooled is employed to cool other portions of the incoming gas before the latter reaches the nozzle. The incoming gas becomes still more cooled after traversing the nozzle. In this way the cooling effect can be made cumulative. In actual practice, this is secured by using either concentric tubes as in Linde's process or by means of Hampson spirals (sec. 21). Two or more concentric tubes are arranged in the form of spirals, the inner one carrying the high-pressure inflowing gas while the outer one the low-pressure outflowing gas. In the regenerative method a further advantage is gained by the fact that the lower the temperature the greater is the Joule-Thomson cooling.

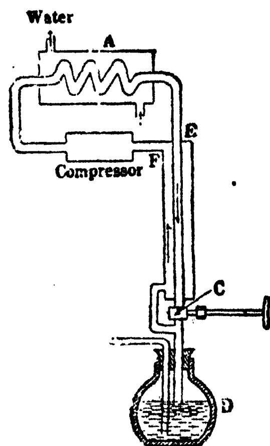


Fig. 10.—Illustration of the Regenerative Cooling.

The regenerative principle is illustrated diagrammatically in Fig. 10 where the high-pressure gas from the compressor enters the spirals contained in the water-cooled jocket A. The gas next enters the regenerator coils at E and by expansion at the valve C becomes cooled by a small amount. This returns by the outer tube abstracting heat from the high pressure gas, and reaches F almost at the same temperature as the incoming gas at E. The gas is again compressed and cooled by A and re-enters at E. As time passes, the gas approaching C becomes cooled more and more, till the Joule-Thomson cooling at C is sufficient to liquefy it *viz.*, its temperature reaches the value at which the gas would liquefy under the pressure prevailing at F. A portion of the escaping gas then condenses inside the Dewar flask D. At this stage the temperature throughout the apparatus becomes steady and may be represented by the curve shown in Fig. 11, p. 142. The part LM represents the continuous decrease of temperature of the gas as we approach the nozzle through the inner tube while MN represents the Joule-Thomson cooling. NL represents the temperature of the low-pressure gas which is less than that of the adjacent high-

pressure gas. Thus the cooler low-pressure gas abstracts heat from the incoming stream.

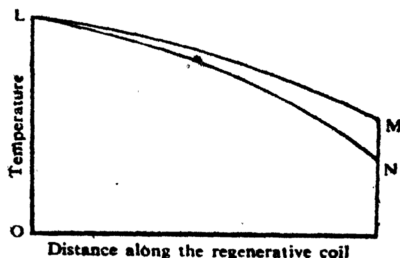


Fig. 11.—Temperature distribution in Regenerative cooling.

20. Linde's Machine for liquefying Air.—The principle of regeneration (applied to heating) was discovered by W. Siemens in 1857, but its application to cooling processes came later. Linde* in Germany and Hampson in England almost simultaneously (1895) built air liquefying machines based on the above principle. At the present time, such machines have become quite common and many laboratories in the world are fitted up with such machines. Fig. 12 shows a commercial form of Linde's machine; *e*, *d*, is a two, or better three

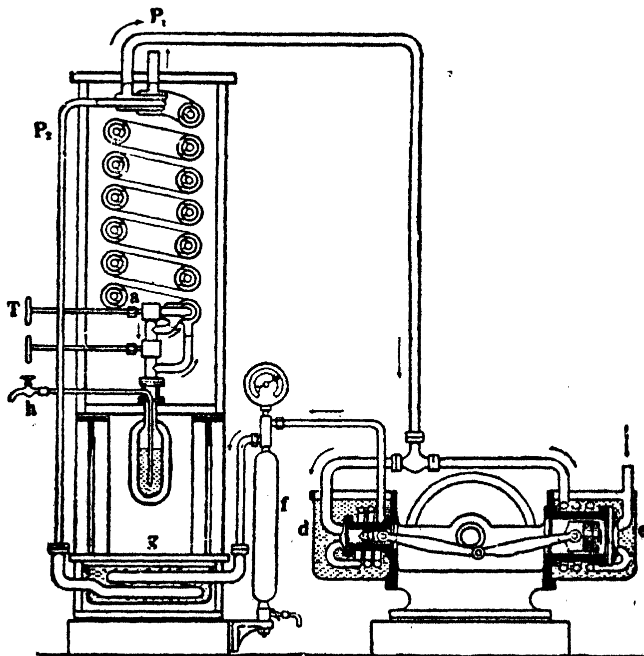


Fig. 12.—Linde's apparatus for liquefying air.

stage compressor, the machine *e* compressing the gas from 1 to 20 atmospheres while *d* compresses it from 20 to 200 atm. A charge of atmospheric air is taken in at *e* and compressed by *e* to 20 atm.

* Karl von Linde, born in 1842, was Professor at Munich. He published an account of his air-liquefying machine in 1895.

It is then cooled by passage through water-cooled tubes and is delivered to the suction side of the second stage compressor. The compressed gas then passes through the cylinder *f* which contains caustic soda. This absorbs the carbon dioxide (if this is not done, carbon dioxide will become solidified and choke the valves in the liquefier proper). The gas then passes to the tubes *g* which are cooled by a freezing mixture to −20°C. From here it passes on through the metallic tubes P_2 to the inner coils of the liquefier proper. At *a* we have got the plug which is a throttle valve operated by the handle T. As the gas expands (in the first stage to 20 atm.), the temperature falls to about −78°C, and the air again passes through the outer coils cooling the incoming gas; it is then led through the pipe P_1 to the second stage compression cylinder, where it is again compressed and allowed to pass through the refrigerator and the inner coils to *a*. After the completion of a few cycles the temperature of the incoming gas falls so low that the second throttle valve is opened. The air is now allowed to expand to 1 atmosphere when it becomes liquid and collects in the Dewar flask, from which it can be removed by the siphon *h*. The unliquefied gas is again led back through the outermost coils to the compressor *e* as indicated by the arrows. Fresh charge of air is being continuously taken in at *e*, compressed and delivered along with the gas from the middle tube to *d*. The process is cyclic.

21. Hampson's Air Liquefier. This liquefier also utilizes the Joule-Thomson effect and the regenerative principle, but differs from Linde's apparatus in details of construction. The special feature about it is the Hampson spiral. The high pressure inflowing gas passes through copper tubes coiled in the form of concentric spirals arranged in layers; it then suffers the throttle expansion and becomes cooled. This cooled air rises through the interstices between the layers of spiral and thereby cools the incoming high-pressure gas. After some time the high-pressure gas becomes sufficiently cooled so that on suffering the throttle expansion, it liquefies. The apparatus thus differs from that of Linde only in the manner of cooling the incoming gas. The apparatus was later improved by Olszewski. The Hampson construction has been utilized later by Dewar, Onnes and Meissner for liquefying hydrogen (see Fig. 14) and helium.

22. Claude's Air Liquefier.—Although the Linde and Hampson liquefiers just described are in extensive use in laboratories and commercial installations, the machines cannot be said to be satisfactory, mainly because the efficiency of the machine, *i.e.*, heat extracted/energy consumed by the machine, is extremely low (about 15%). The cooling process employing Joule-Thomson expansion is really very inefficient. A more efficient machine could be devised if the compressed gas was made to expand adiabatically doing external work and thereby suffered cooling. The technical difficulties in constructing an apparatus for continuous liquefaction of gases by adiabatic expansion were overcome by Claude. The main difficulty consists in finding a suitable lubricant for the moving parts of the expansion cylinder since the ordinary lubricants become solidified at these

low temperatures. Claude utilized petroleum ether as the lubricant This remains viscous at temperatures of −140°C. or even −160°C and thus acts as an effective lubricant up to this range.

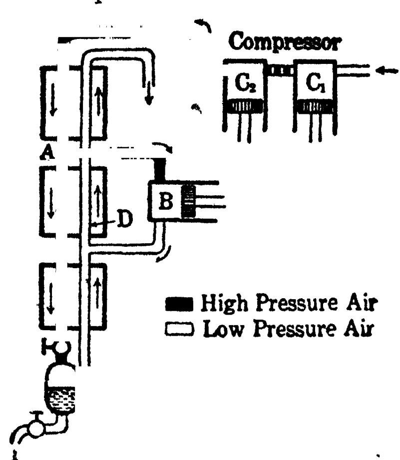


Fig. 13.—Claude-Heylandt system.

Fig. 13 shows diagrammatically the Claude's air liquefying machine. The gas from the compressor is divided into two parts at A. One part goes to the expansion cylinder and suffers adiabatic expansion and consequent cooling. In this expansion it does external work which is utilized in doing work on the compressor. The cooled gas traverses upwards in the pipe D thereby cooling the second part of the incoming compressed gas in the second heat-exchanger. The high-pressure gas thus partially liquefies. It then suffers Joule-Thomson expansion at the throttle valve. The evaporated gas is taken to the compressor and again compressed.

Theoretically Claude's method should be more efficient than the Linde process but in actual practice it is only slightly so. This is due to the serious technical difficulties of the Claude method. The Linde method has the great advantage that no movable parts of the apparatus are at low temperatures and hence the construction is simple. Heylandt slightly modified the Claude liquefier.

It is obvious that an expansion turbine will possess several advantages over the reciprocating engine. Kapitza in 1939 developed an air liquefier in which the compressed air is allowed to expand from a pressure of about 5 atmos. to a pressure of about 1·5 atmos. and drive a turbine wheel, and thereby suffer cooling on account of the work done. The machine is about three times as efficient as Linde's liquefier and as it utilizes a pressure of about 5 atmospheres only, all danger due to high pressure is eliminated.

23. Liquefaction of Hydrogen.—The method of cascades failed* to liquefy hydrogen. Wroblewski thereupon studied the isotherms of hydrogen at low temperatures, and from that calculated the values of a and b, and thence the critical constants (p. 95). The critical temperature was found to be very low (−240°C.) and Olszewski pointed out that this temperature could not be reached by the evaporation of liquid nitrogen, which was the most intensive cooling agent then known. The physicists then turned to the Joule-Thomson method.

This method, however, first appeared to be inapplicable to hydrogen and helium, for Regnault had shown that when hydrogen

* Neon can be utilised but it is very rare.

is subjected to this process, it gets heated instead of being cooled. That the difficulty is not fundamental and insuperable can be seen from the expression for the Joule-Thomson effect *viz.*,

$$\frac{\triangle\theta}{\triangle p} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right). \quad . \quad . \quad . \quad . \quad (4)$$

It is thus proportional to $2a/RT - b$ but in hydrogen and helium a is so small that at ordinary temperatures $2a/RT < b$, and the term on the right-hand side becomes negative. Hence, for a negative value of $\triangle p$, *i.e.*, expansion of the gas, $\triangle\theta$ is positive at ordinary temperatures, and the gas shows a heating effect.

If T be sufficiently reduced, the right-hand term in (4) eventually becomes positive and the gas shows a cooling effect. There is just a temperature where $2a/RT - b = 0$, *i.e.*, where Joule-Thomson effect changes sign; this temperature is called the '*temperature of inversion*' T_i, which is thus equal to $2a/bR$. This relation gives, after substituting the values of a and b for hydrogen, T_i to be $-73°$C. Olszewski experimentally observed the Joule-Thomson effect for hydrogen at various temperatures and found the temperature of inversion to be $-80{\cdot}5°$C.

Similar is the case with all gases. There is a temperature of inversion for all of them which, however, depends upon the initial pressure of the gas. Even the Joule-Thomson effect depends very much upon the initial pressure. It is thus clear that the behaviour of hydrogen and helium is not anomalous; they differ from other gases only in having a low temperature of inversion.

Now since T_c, the critical temperature, is equal to $8a/27bR$ (p. 95) and $T_i = 2a/bR$, it follows that $T_i = (27/4)T_c$. This relation is found to hold true approximately.

Hydrogen must, therefore, be cooled below $-80°$C. for liquefaction. But for practical success it should be pre-cooled to the Boyle point T_B (p. 88) which is defined as the point at which $\frac{\partial(pV)}{\partial p} = 0$. Calculation with the help of van der Waals' equation shows that this temperature $T_B = a/bR$. Hence $T_B = \frac{1}{2}T_i$. We thus see that hydrogen should be pre-cooled to about 96°K ($-177°$C). This temperature is easily attained if we immerse the hydrogen liquefying apparatus in a bath of liquid air.

24. Hydrogen Liquefying Apparatus.—Dewar first succeeded in liquefying hydrogen in this manner in the year 1898. Travers later improved the apparatus. Hydrogen prepared from zinc and sulphuric acid is compressed to about 150 atm. and then passed through coils immersed in water in order to deprive the gas of the heat of compression. Next it passes through cylinders of caustic potash and some dehydrating agent and is deprived of its carbon dioxide and moisture. This is essential as these impurities would solidify much before the liquefaction of hydrogen sets in and choke the tubes. The

gas then enters the liquefier and traverses the regenerative coils A (Fig. 14) which are cooled by the outgoing cold hydrogen gas, and in the final steady state, becomes cooled to about −170°C. Next the gas passes through a refrigerating coil B immersed in liquid air, and then through another refrigerating coil C immersed in liquid air boiling at a pressure of 100 mm. This is adjusted by allowing liquid air from F to trickle into G and by evacuating G through a pump attached at P. The temperature of the hydrogen gas thus falls to about −200°C. After this it traverses the coil D and suffers Joule-Thomson expansion at the valve *a* which is operated by H. The gas thus becomes cooled and this cold gas passes up round the chambers G and F, thereby cooling the coils D and C, to the chamber R and from there to the compressor. Thus after a few cycles the temperature of the incoming gas at *a* falls to −250°C, and then on suffering the Joule-Thomson expansion it liquefies and drops as liquid into the Dewar vessel V.

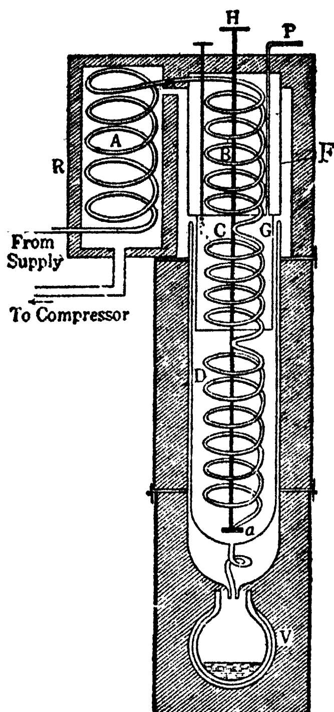


Fig. 14.—Hydrogen liquefier.

Many later investigators devised apparatus which have a large output. Amongst them may be mentioned Nernst, Kamerlingh Onnes and Meissner. Onnes' apparatus is very similar to his helium liquefier. Meissner's apparatus is somewhat different in construction but similar in principle.

Liquid hydrogen boils at −252·78°C. under atmospheric pressure. By causing it to boil under reduced pressure it can be frozen to a white solid.

25. Liquefaction of Helium.—Helium could not be liquefied for a long time. The attempts of Dewar and Olszewski to liquefy helium by the adiabatic expansion method were unsuccessful. Kamerlingh Onnes,* however, proceeded in his efforts very systematically. He studied the isotherms of helium down to liquid hydrogen temperatures (up to −250°C) and obtained the critical constants for helium. He found the following values:—$T_c = 5{\cdot}25°K$, $p_c = 2{\cdot}26$ atm. and normal boiling point = 4·26°K. The Joule-Thomson inver-

* Heike Kamerlingh Onnes (1853—1926), born in Holland, became Professor of Physics at Leiden where he established his low temperature laboratory and investigated the properties of substances at low temperatures.

sion point came out to be about 35°K and the Boyle point 17°K. This temperature could, therefore, be reached by pre-cooling the gas with liquid hydrogen. Kamerlingh Onnes was thus convinced of the possibility of being able to liquefy helium by the Linde process. He succeeded in actually liquefying it in 1908 in his laboratory at Leiden. Subsequently helium liquefiers were constructed at Leiden, Berlin and Toronto. To-day there are scores of helium liquefiers in the world. Since helium is rather costly, the arrangement should be such that it can work in cycles. In the apparatus used at the cryogenic laboratory at Leiden gaseous helium compressed to 36 atm. is passed through spirals immersed in liquid hydrogen boiling under reduced pressure and then through outgoing cold helium vapour. The gas then suffers Joule-Thomson expansion and becomes liquefied. The plant for liquefying helium is, therefore, complicated by arrangements for liquefying air and hydrogen.

Both hydrogen and helium were liquefied by Kapitza in 1934 by the Claude-Heylandt method. Helium was liquefied by Simon by the adiabatic expansion method and also by the desorption method. Collins in 1947 developed a commercial type of helium liquefier based on the Kapitza method. In the Collins expansion engine the piston and cylinder are constructed of nitrided nitralloy steel, the clearance being about 0·0005 inches on the diameter and the operation being completely dry. Thus the leakage of gas is extremely small and whatever does leak, also goes to the suction side of the compressor.

26. Solidification of Helium.—Kamerlingh Onnes tried to solidify helium by boiling it under reduced pressure, but though he claimed to have reached 1·15°K in 1910, helium still remained a fluid. In 1921 he again tackled the problem and by employing a battery of large diffusion pumps he reduced the vapour pressure to 0·013 mm. and the temperature to 0·81°K, but helium still remained fluid. After the death of Onnes, his collaborator and successor, Dr. Keesom succeeded in 1926 in solidifying helium by subjecting it to an enormous pressure. Helium was compressed in a narrow brass tube under a pressure of 130 atmospheres, the tube itself being immersed in a liquid helium bath. It was found that the tube was blocked indicating that part of the gas had solidified. If the pressure was reduced by 1 or 2 atmospheres, the tube became clear again. Later experiments showed that helium at 4·2°K solidified at 140 atmospheres while at 1·1°K it solidified only under 23 atmospheres. Solid helium can hardly be distinguished from the liquid: it is a transparent mass having almost the same refractive index as the liquid.

27. Cooling produced by Adiabatic Demagnetisation.—Upto 1925 the only method available for producing temperature lower than 4°K was the boiling of liquid helium under reduced pressure. Keesom in this way reached 0·72°K in 1932. In 1926 Debye and Giauque showed theoretically that lower temperatures could be produced by the adiabatic demagnetisation of paramagnetic substances (i.e. those substances for which the magnetic susceptibility χ is small but positive). The principle of the method is as follows:—

The process of magnetising a substance involves doing work on it in aligning the elementary magnets in the direction of the external field. If a substance already magnetised is demagnetised adiabatically, it has to do work and the energy to do this work is drawn from within itself, in consequence of which it cools. This cooling can be made large if a strong magnetic field is employed and the initial temperature is low because then the magnetisation produced in the substance is large. This follows from Curie's law which states that the paramagnetic susceptibility of a substance varies inversely as the absolute temperature i.e. $\chi = C/T$. The final temperature attained is determined by measuring the magnetic susceptibility of the substance and calculating from Curie's law. In this way de Haas and Wiersma succeeded in reaching the present low temperature record of about 0·0034°K in 1935 by adiabatically demagnetising mixed crystals of chromium-potassium alum and aluminium-potassium alum at 1·29°K from an initial field of 24000 gauss.

28. Properties of substances at liquid helium temperatures.— Properties of substances undergo very interesting changes at extremely low temperatures. K. Onnes found in 1911 that at about 4°K many metals appear to lose completely their electrical resistance and become superconducting. The resistance does not absolutely vanish but falls to about a millionth of its value so that if a current be induced in a coil of the metal placed inside such a low temperature bath by bringing a magnet near it, the current does not immediately die out as in ordinary electromagnetic induction, but may continue to flow for days together. It has also been found that near the absolute null-point, the specific heat seems to vanish. Besides, liquid helium itself below about 2°K possesses strange properties, the most important being the property of superfluidity when the liquid has no viscosity.

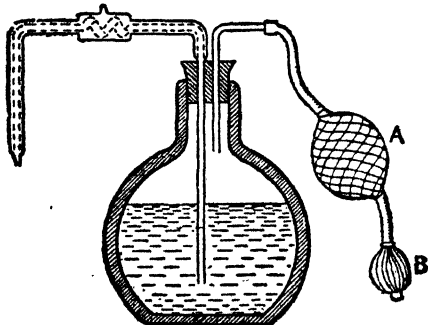


Fig. 15.—Dewar Flask.

29. Low Temperature Technique.—*Dewar flask.*—The discovery of Dewar flask by Sir James Dewar* in the Royal Institution of London provided a very convenient apparatus for low temperature storage. Though very low temperatures had been produced, it was difficult to maintain the liquids at these temperatures as even by packing the bottles with the best heat insulating material, the leakage of heat from outside could not be prevented. But the problem was solved by Dewar in a very ingenious way.

* James Dewar (1842-1923), born at Kincardine, became Professor of Natural Philosophy at Cambridge in 1875 and also Professor of Chemistry in the Royal Institution in 1877. His chief work was in the low temperature region.

The Dewar flask (shown in Fig. 15 together with a siphon) consists of a double-walled glass vessel, the inside walls being silvered. The air is completely evacuated from the interspace between the walls which is then sealed. If some substance be now placed inside such a vessel and the top closed, it is perfectly heat insulated, except for the small amount of heat which may creep in by conduction along the sides. The silver coatings protect the inside from radiation, and the absence of air prevents the passage of heat by conduction through the walls. If the substance be hung by thin wires inside the flask and the latter evacuated by pump and sealed, the insulation is complete. Such an arrangement was used by Nernst in his low temperature calorimetry (p. 42). Dewar flasks are now sold in the market under the trade name "Thermos flask". They have lately been made entirely of metal with a long neck of some badly conducting alloy as German silver.

Low Temperature Siphons.—For transferring liquid air from one vessel to another, special types of siphons are used. One such siphon is shown in Fig. 15, connected to the Dewar flask. It is formed of a double-walled tube silvered inside, the space between the walls being evacuated. On the application of gentle pressure to the rubber compressors A or B, liquid air rises up the siphon and can be transferred to a second vessel.

Cryostats.—For low temperature work constant temperature baths are necessary; they are called cryostats. The substance to be investigated is kept immersed in these baths. From Table 3, (p. 136) it is easy to find out which liquids are suitable in a particular range of temperatures. In this way suitable liquid baths can be easily constructed down to $-218°C$. When no suitable liquids are available, vapours of liquids can be employed.

30. Uses of Liquid Air and Other Liquefied Gases.—The importance of liquid air is being increasingly felt so much so that it has now become essential for several purposes. Bottles of liquid air can now be obtained in any important modern town at a comparatively small cost. We shall give some of the important uses to which liquid air has been put.

(i) Production of High Vacuum.—High vacuum can be obtained by using liquefied gases with or without charcoal. For instance, if a vessel is first filled with a less volatile gas than air, say sulphurous acid or water vapour, and is then surrounded by liquid air all the gas inside becomes solidified and thus high vacuum is produced. If the vessel contains air, liquid hydrogen may be employed to condense it. This process is greatly assisted by charcoal which possesses the remarkable property of occluding gases at very low temperatures and the lower its temperature the greater is the adsorption. Further also the adsorption is selective; as a general rule it may be said that the more volatile the gas, the less it is adsorbed.

We shall give a numerical example. During a certain experiment a vessel containing air at a pressure of 1·7 mm. at 15°C., when

cooled by charcoal immersed in liquid air, gave a pressure of 0·000047 mm. in an hour and using liquid hydrogen as the cooler the pressure was reduced to 0·0000058 mm.

(*ii*) *Analytical Uses of Air.*—Liquid air is of great use in drying and purifying gases. Water vapour and the less volatile impurities are easily removed by surrounding the gas in question (say H_2) with liquid air, and for this purpose it is now used as a common laboratory reagent.

(*iii*) *Preparation of Gases from Liquid Air.*—Oxygen is now prepared commercially from liquid air by fractional distillation. Since the boiling point of nitrogen is $-195·8°$C., and that of oxygen is $-182·9°$C., the fraction to evaporate first will be rich in nitrogen while that evaporating last will be rich in oxygen. A few fractional distillations will suffice to separate these completely. Several rectifiers have been devised to effect this separation. In Linde's rectifier (1902) liquid air trickles down a rectifying column where it meets an upgoing stream of gas. The temperature at the top of the column is slightly below $-194°$C. (B.P. of liquid air) while at the bottom it is $-183°$C. (B. P. of oxygen). The rising gas at the bottom comes in contact with the down-coming liquid and thereby some oxygen of the rising gas is condensed, while some of the nitrogen in the downcoming liquid evaporates, and the liquid also becomes warmer. The process continues till the liquid reaches the bottom when it contains nearly pure oxygen, while nitrogen passes off as vapour at the top. This oxygen is almost pure but the nitrogen contains about 7% of oxygen. More efficient rectifiers have since been devised by other workers. For details see *Separation of Gases* by M. Ruhemann, Chaps. VI, VII and VIII.

Again atmospheric air may be utilised for the production of the rare gases, particularly helium, neon and argon. Roughly five volumes of helium are found in million volumes of air but this is sufficient for our purpose. Liquid air may be separated into two fractions, the less volatile part consisting of O_2, N_2, A, CO_2, Kr, Xe and the more volatile part consisting of He, H_2, Ne. Thus in the rectifier described above the gas going up will contain N_2, H_2, He and Ne. The nitrogen is removed by passing the gas through a dephlegmator and hydrogen is removed by sparking with oxygen. Neon and helium can be separated by cooling the mixture with liquid hydrogen. Thus, oxygen, nitrogen and helium may be obtained from air. For details see Ruhemann, *Separation of Gases*, Chap. IX.

(*iv*) *Calorimetric Applications.*—Dewar constructed calorimeters of liquid air, oxygen and hydrogen. He employed pure lead as the heater, and the volume of the gas evaporated by the application of this heat was measured. These calorimeters have the advantage that a large quantity of gas is formed which makes it possible to detect as little as 1/300 calorie with liquid hydrogen. In this way

the specific heat of lead and other substances may be investigated at low temperatures.

(*v*) *Use of Liquid Gases in Scientific Research.*—The extremely low temperatures which are now available to us by the use of liquid air and liquid hydrogen have opened for the investigator a new and vast field for research. This has made a liquid air plant essential for every modern laboratory. Most of the important properties of matter have been investigated at low temperatures and have yielded results of far-reaching importance. This has been extended even to biological research, where it has been shown that bacteria as well as seeds retain their activity unimpaired even after exposure to liquid air temperatures though a moderately high temperature is fatal.

(*vi*) *Industrial Uses of Liquid Gases.*—Liquid air is used commercially for the preparation of liquid oxygen as explained above. For submarines and aeroplanes it may be found useful to store liquid air or liquid oxygen for respiration but the low thermodynamic efficiency inherent in the Linde machine prevents the use of liquid air in a heat engine (Chap. IX) on any large scale, though mixtures of liquid oxygen and liquid hydrogen have been successfully used as a highly efficient light-weight fuel for jet-propelled aero-engines. Liquid oxygen is, employed on a small scale for preparing explosives, for when mixed with powdered charcoal and detonated, it explodes with great violence.

31. Principles of Air-conditioning.—*The Comfort Chart.*—The seasonal variations of temperature, humidity, etc., have marked effect on growth, longevity and working efficiency of man. The seasonal changes of the year lead us to change periodically our clothing, food and manner of living. But we can hardly cope adequately with the variations unless we can really control the weather changes within our comfort limits as regards temperature, humidity and other factors. The science of refrigeration, heating and ventilating devices have rendered it possible to control the weather at least within the four walls of our room. This particular branch of study is known as the science of air-conditioning.

Complete air-conditioning means the control of the following factors:

	Average comfort condition.
(i) Temperature	75-77°F.
(ii) Relative Humidity	60-65%.
(iii) Air movement	25—75 ft./min.
(iv) Introducing Fresh Air	at least 25% of total circulation.
(v) Purification of Air	
(vi) Deodorizing	
(vii) Ionization or Activating the Air.	

Although apparently temperature seems to be the only guiding factor in the comfort feeling, the relative humidity (r.h.) plays almost equally important role in the feeling of warmth. The same tempera-

ture condition, say 75°F. may make us feel either a bit too warm or too chilly according as the r.h. is too high or too low. This is because the humidity condition controls the evaporation from our body and hence the abstraction of latent heat which gives rise to the different warmth feeling. It is interesting to note that some of the air-conditioning plants in the tropics (Calcutta) do not employ any heating device during winter but only humidify the atmosphere by atomised spray of water. This is because the average winter temperature of the place (about 70—75°F indoors) is not really too low, but what makes us feel chilly is the low (40%) r.h. So we feel quite comfortable only by raising the r.h. up to 60—70%. In cold countries, however, rooms are conditioned by electrical or steam-pipe heating devices.

It is interesting to find that the comfort feeling is fairly critical, that is to say, that individual variation does not go much off the average. Elaborate experiments have been performed by the Harvard School of Public Health in collaboration with the American Society of Heating and Ventilating Engineers on the average comfort feeling under the different combinations of temperature, humidity and air

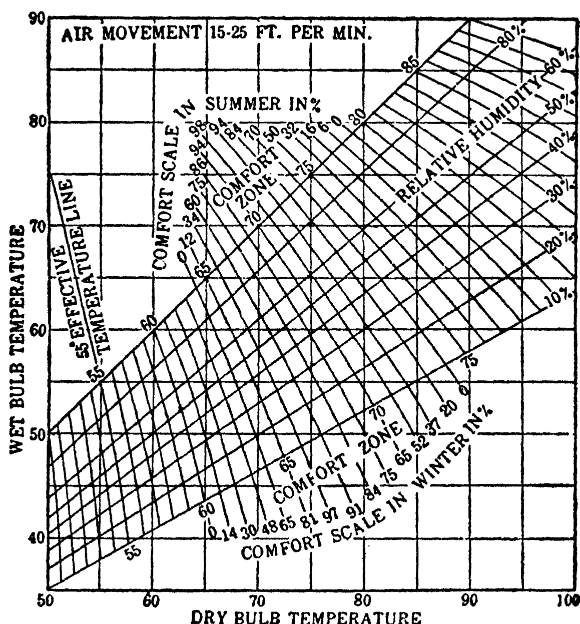


Fig. 16.—The comfort chart.

velocities, etc. As a result of these experiments the comfort chart (Fig. 16) is drawn in which the co-ordinates are the dry and the wet bulb temperatures and lines of constant r.h. and comfort scales for

summer and winter are also drawn. The chart shows that 98% of the people during summer would feel very comfortable at 71°F. effective temperature. We shall see presently what effective temperature really means. It relates to the human feeling of warmth under various combinations of temperature, r.h. and air velocity. For example, this 71°F effective temperature, may be obtained by various combinations, such as 40% r.h., 78°F dry bulb, 62°F wet bulb ; or 60% r.h., 75°F dry bulb, 60°F wet bulb ; or 70% r.h., 74°F dry bulb, 67°F wet bulb (all with air velocities 15—25 ft./min.). So we see that the term 'effective temperature' represents a new scale which enables us to standardise the comfort feeling due to the various combinations of dry bulb and wet bulb temperatures (which automatically define r.h.) and air movements. The three combinations (starting with 40%, 60% and 70% r.h.,) as exemplified above would give rise to a feeling as if the person were placed at a temperature of 71°F in a saturated atmosphere and with still air. This is how we can define effective temperature.

The effective temperature scale thus represents the conditions of equal warmth feeling with various combinations of temperature, humidity and air movements. These are findings based on experiments with men and women with normal clothing and activity and subjected to conditioned atmospheres of the various combinations of temperature, r.h., and air movements.

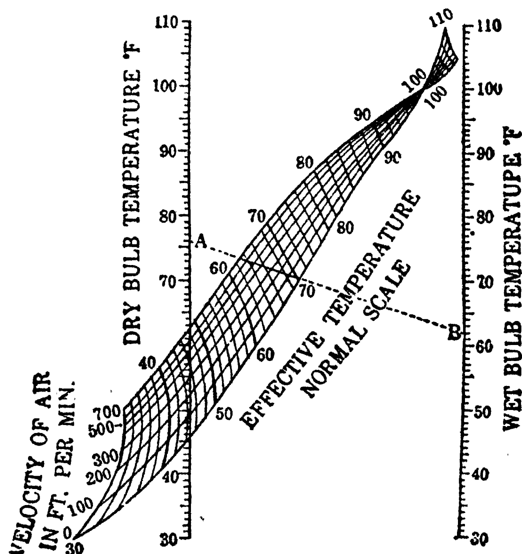


Fig. 17.—Effective temperature chart.

Fig. 17 shows the effective temperature chart. Let us see how to read the chart to find the effective temperature. Suppose that we have in the room an atmosphere with dry bulb temperature 76°F, and wet bulb 62°F and wind velocity 30 ft./min. (0-30 ft./min. may be taken as good as still air.) Now put the straight edge of a scale across the two temperatures (the dotted line), and it intersects the effective temperature lines at about 70°F. If the same temperature of 76°F dry bulb and 62°F wet bulb are found to exist with a wind velocity of 200 ft./min. our feeling would be corresponding to 67½°F effective temperature and so on.

We have seen that temperature and humidity are the most important factors for comfort feeling, while movement of air gives

a feeling of ease if it has velocities within 25-75 ft./min. If the air is dead still, it becomes uncomfortable and stuffy. On the other hand, if it has too high a velocity it becomes blasty and we would not like it. The higher the wind velocity, the colder is our feeling, as it facilitates evaporation from our body.

We next consider fresh air. A room-cooler (or a room-heater in the cold season) must make provision for introducing sufficient amount of fresh air into the room. Of the total circulation a minimum of 25% fresh air is recommended, the remaining part is the room air itself, recirculating through the machine. It is true that if more air is drawn from outside and cooled in the air-conditioning machine for distribution in the room it were better, but it becomes too expensive since much more work has got to be done in order to cool the large bulk of outside hot air.

In a complete air-conditioning outfit, devices are included to purify and deodorize the air by suitable means.

In spite of the complete air-conditioning arrangements it is found that we can never feel like the natural atmosphere under the same conditions. Recently it has been found that the amount of electrically charged ions present in fresh atmosphere is higher than that present in the air of an occupied room. Experiments have been made to ionise air by X-rays and introduce the ions into the room in natural proportions to activate the atmosphere of the room. This has given positive effect.

32. The Air-Conditioning Machine.— We have so far seen what 'air-conditioning' actually means. We shall now consider how it is achieved.

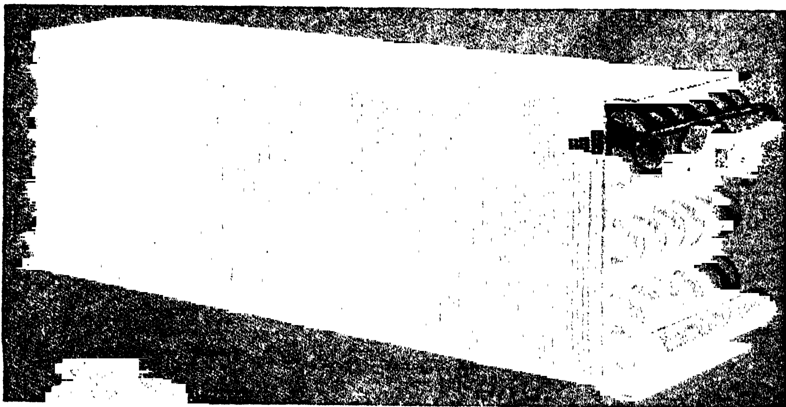


Fig. 18.—The Evaporator.

The air-conditioning machine or the room-cooler is fundamentally a refrigerating machine which has been described in section 7, p. 130 with the main difference in the design of its evaporators. This is

just the question of how we want to utilize the cold produced by the refrigerating machine. In air-conditioning unit the evaporator consists of a series of zigzag copper-tubings thoroughly finned with thin copper sheets in order to get a large area of cold surface (Fig. 18). As the liquefied refrigerant (SO_2, Freon, etc.) evaporates in the tubing at low pressure, it becomes cooled and a fan put behind the evaporator drives the warm air in the room. A complete frigidaire-conditioner is shown in Fig 19 with the fan, cooling and heating coils, humidifier, etc., clearly shown.

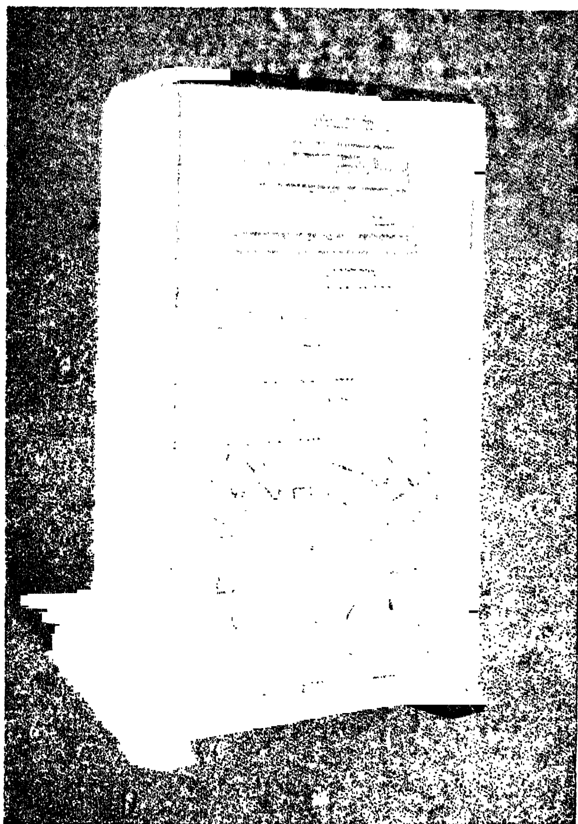


Fig. 19.—Frigidaire conditioner.

It is important to note that the summer air is laden with much moisture and it is desirable that humidity should be lowered. As the air is fanned through the cold fins of the evaporator the moisture condenses on them into droplets which are ultimately drained off. Thus cooling and dehumidification are simultaneously brought about in the same process.

The size and capacity of an air-conditioning machine is not determined only by the size of a room. It depends upon the following considerations of heat loads :

(*i*) Sun's rays falling on walls or roof.
(*ii*) Conduction through walls and roofs due to the difference of outside and inside temperatures.
(*iii*) *Human occupancy.*—For small private installations this heat load is not more than 5% of the total load but in cinema or theatre halls, it is 55 to 65% and in restaurant 40 to 60%. (Average heat dissipation is taken to be 400 B.t.u per hour by each person).
(*iv*) Infiltration, *i.e.*, outside unconditioned air entering through conditioning machine itself (its motor), cooking stove, etc.
(*v*) Heat-producing items in the room, *e.g.*, electric lamps, air-conditioning machine itself (its motor), cooking stove, etc.

In order to minimise the heat load which mostly enters from outside, the walls and ceiling must be covered with insulating boards such as celotex, masonite, etc. and matting for the floor should be used.

It should, however, be noted that the comfort feeling varies to some extent for people of different countries. The comfort chart shown in Fig. 16, is suitable for people of temperate climates, like America and most of the European countries. But for tropical countries like India, the chart would differ considerably. People in the tropics are accustomed to more warmth and humid atmosphere, and this is why the American air-conditioning machines have got to be readjusted according to our comfort conditions.

Books Recommended.

1. Andrade, *Engines.*

2. L. C. Jackson, *Low Temperature Physics* (1950), Methuen & Co.

3. M. and B. Ruhemann, *Low Temperature Physics* (1937), Cambridge University Press.

4. C. F. Squire, *Low Temperature Physics* (1953), McGraw-Hill Book Co.

5.. M. Ruhemann, *The Separation of Gases*, (1940), Clarendon Press, Oxford.

6. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, articles on 'Refrigeration' and 'Liquefaction'.

7. Moyer and Fittz, *Refrigeration.*

8. Hull, *Household Refrigeration*, Published by Nickerson & Collins Co., Chicago.

9. K. Mendelssohn, *Cryophysics*, (1960), Interscience Publishers, Inc., New York.

CHAPTER VII

THERMAL EXPANSION

1. The size of all material bodies changes on being heated. In the majority of cases, the size increases with rise in temperature, the important exceptions being water and some aqueous solutions in the range 0 to 4°C, and the iodide of silver (resolidified) below 142°C. We shall first consider the expansion of solids.

EXPANSION OF SOLIDS

2. The cubical expansion of solids is somewhat difficult to measure directly (a method is given in section 17), and is generally calculated from the linear expansion. Hence, experiments on the expansion of solids generally consist in measuring the linear expansion of bars or rods of the solid. For isotropic bodies whose properties are the same in all directions, the expansion is also the same in all directions. To this class belong amorphous solids (e.g., glass) and regular systems of crystals (*e.g.*, rock salt). Metals may also be included because though they are composed of a very large number of small crystals, these crystals are oriented at random and the *average* properties are independent of direction. In anisotropic bodies such as many crystals, the expansion is different in different directions and may be even of different sign. We shall first consider isotropic bodies.

ISOTROPIC SOLIDS

3. Linear Expansion.—If a bar of length l_0 at 0°C. occupies a length l_t when raised to t°C., l_t can always be expressed by a relation of the form

$$l_t = l_0(1+\lambda t), \quad . \quad . \quad . \quad (1)$$

where λ is called the mean coefficient of linear expansion between 0 and t°C., and is a very small quantity. This differs very little from the true coefficient of linear expansion α at the temperature t which is equal to $\frac{1}{l}\frac{dl}{dt}$. The true coefficient α may also be defined by the relation $\alpha = \frac{1}{l_0}\frac{dl}{dt}$ which on integration will yield (1) if $\int \alpha dt = \lambda t$. The mean coefficient λ may be put equal to the coefficient of expansion at $t/2$ °C if the range of temperature is small. Often the initial length is measured not at 0°C but at t_1°C. Then if t_2 denotes the other temperature at which the length is l_2, we have

$$\frac{l_2}{l_1} = \frac{1+\lambda t_2}{1+\lambda t_1} = 1 + \lambda(t_2 - t_1) \text{ approx.}$$

by the binomial expansion. Hence

$$\lambda = \frac{l_2 - l_1}{l_1(t_2 - t_1)} \text{ approx.} \quad . \quad . \quad . \quad (2)$$

The mean coefficient λ itself is found to vary with temperature. This implies that the relation connecting length and temperature is not a linear one and equation (1) must be modified into

$$l_t = l_0 \ (1 + \lambda_1 + \lambda_2 t^2 + \ldots), \quad . \quad . \quad . \quad (3)$$

where the successive coefficients go on decreasing rapidly. An equation of this type is entirely empirical. The molecular theory of matter has not yet been developed sufficiently to yield an exact theoretical formula. Generally it is sufficient to include terms up to the square of t; the relation then becomes parabolic. In most cases both the coefficients λ_1 and λ_2 are positive, the body becoming more expansible as the temperature rises.

4. Earlier Measurements of Linear Expansion.—The linear expansion of solids is very small; a bar of iron one metre long when heated from 0 to 100°C., increases in length by about 1·2 mm. To measure such small changes in length accurately, special devices are necessary. The increase in length may be obtained from the readings of a spherometer, or directly observed by means of a microscope. Again, the expansion may be multiplied in a known ratio by utilising the principle of the lever. The most satisfactory method, however, consists in utilising the interference fringes, which is considered in detail later. In this section, we shall consider the earlier experiments.

The spherometer or a *micrometer screw* was generally employed to measure the expansion and is suitable for ordinary work. The experimental bar, about a metre long, has its one end pressed against a fixed screw while the other end is free to expand. There is a micrometer screw or a spherometer which can be brought into contact with this end. By noting the micrometer readings when the screw is in contact at 0°C., and at any other temperature t°C., the expansion of the rod is found, whence the mean coefficient of linear expansion can be calculated from equation (1).

Roy and Ramsden employed *microscopes* to measure the expansion and were able to obtain results of considerable accuracy. The experimental bar was placed horizontally in a trough between two standard bars, and parallel to them. One standard bar carries a cross-mark at each end while the other carries at either end an eye-piece provided with cross-wires. The experimental bar carries an object glass at both ends so that the eye-piece on the standard rod and the object glass on the experimental bar together formed a microscope focussed on the cross-mark on the second standard bar. The standard bars were always kept in ice. One end of the experimental bar was fixed while the other end was free to move when the bar was heated. The object glass was brought back to its initial position by a fine micrometer screw, whose initial and final readings gave the expansion.

Laplace and Lavoisier employed the lever principle to magnify the expansion (*mechanical lever method*). The change in length was converted into a change in angle by means of a lever arrangement and the angular change was measured by a scale and a mirror or telescope. The principle of their apparatus is indicated in Fig. 1. One end A of the experimental bar AB is fixed while the other end B pushes against a vertical lever OB attached at right angles to the axis of a telescope LL, which is itself pivoted at O and is focussed on a distant vertical scale CC′. The bar AB is first placed in melting ice and the scale division C seen through the telescope is noted. Next the bar is enclosed in a hot-water bath. The rod AB expands to B′ thereby tilting the telescope LOL to the position L′OL′ and the scale division C′ is now seen through the telescope. The expansion BB′ is equal to OB tan $\angle$ BOB′ = OB tan $\angle$ COC′ = OB × CC′/OC.

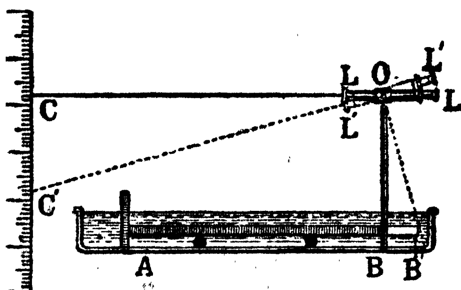


Fig. 1.—Apparatus of Laplace and Lavoisier.

Paschen employed a combination of the micrometer screw and the lever. The expansion was multiplied in the ratio 1:5 by the lever and this magnified change in length was measured by the micrometer screw. An optical lever arrangement is also sometimes used when the expansion causes a plane mirror to tilt and thereby deflect a ray reflected from the mirror.

5. Standard Methods.—At the present time the standard methods employed for measuring expansion are:

(1) Comparator Method, (2) Henning's Tube Method, (3) Method of Interference Fringes. Methods (1) and (3) are direct while (2) is indirect.

6. Comparator Method.— This is a standard precision method for determining the expansion of materials in the form of a bar or tube. The bar, about a metre long, is mounted horizontally in a double-walled trough so that it can expand freely at both ends (Fig. 2) and has two fine marks L, L made near the ends. A standard metre is also mounted horizontally in another double-walled trough, both these troughs being arranged parallel to each other and mounted on rails so that either the experimental bar or the standard metre can be brought into the field of view of two vertical microscopes M, M. The microscopes are provided with an eyepiece micrometer or can be moved parallel to the direction of expansion by means of a micrometer screw, and are fixed vertically in rigid horizontal supports projecting out from two massive pillars, the distance between the microscopes being about one metre.

First the two troughs are filled with water surrounded by melting ice in the space between the double walls. The experimental bar is then wheeled into position and the fine marks on it are viewed

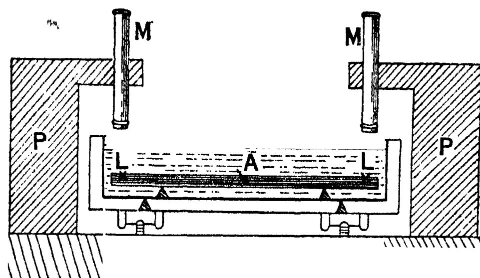


Fig. 2.—The Comparator method.

through the two microscopes and their positions are noted in the micrometer. The standard metre is then brought below the microscopes and the two extreme marks of graduation are viewed through the microscopes. From the change in the micrometer reading the length of the bar at 0°C is obtained. The experimental bar is then heated by replacing the melting ice in the double-walled space of the trough by water which is heated under thermostatic control. The fine marks are again viewed through the micrometer eyepiece. The increase in length is determined from the change in micrometer reading. For measurements at low temperatures the experimental rod is placed in a tube which is immersed in a suitable liquid bath (*e.g.* liquid air).

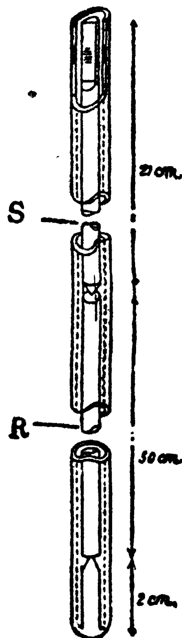


Fig. 3.—Henning's apparatus.

7. Henning's Tube Method of Measuring Relative Expansion.—In this method the experimental and the comparison bodies are together brought to the same temperature and the differential change of their lengths is measured. The comparison body is so chosen that its expansion in the temperature region is accurately known and, if possible, is also very small. Fused silica serves this purpose well. Inside a long vertical tube made of some well-defined glass (fused silica, Jena glass), there is a ground point, molten and drawn out of the same glass at its lower end. Upon this point rests the experimental rod R (Fig. 3), about 50 cm. long and having both of its end faces ground plane. Upon the upper surface of R rests a pointed end of another glass rod S made of the same glass as the outer wider tube. To the upper end of this rod as well as of the outer tube are attached end-pieces carrying scales. The whole tube

up to half of the height of the rod S is immersed in a hot or cold bath and the relative shift of the end-pieces is measured with a microscope provided with a micrometer eyepiece. The shift gives the relative expansion of the experimental rod against a glass tube of equal length. This is so on the assumption that the temperature of the rod and of the outer tube is the same at the same height. For high and low temperatures suitable baths may be employed.

8. Fizeau's Interference Method.—Fizeau devised an optical method depending upon the observation of interference fringes. This method is capable of very great accuracy and is specially suitable when small specimens of the experimental substance are available, as in the case of crystals.

In his original experiment, Fizeau used the substance B (Fig. 4) in the form of a slab about 1 cm. thick with two of its opposite plane

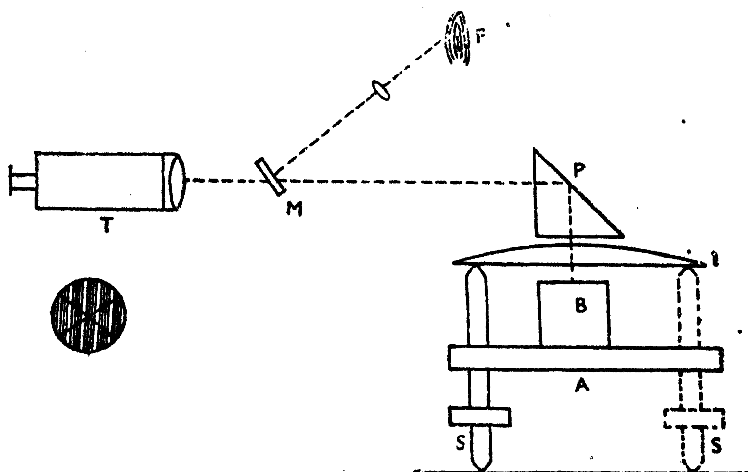


Fig. 4.—Fizeau's interference method.

faces parallel and polished. It was placed with one of these faces horizontal on a metal plate A supported by three levelling screws S, S. These screws projected upward through the metal plate a little beyond the upper surface of the slab B. A convex lens L having the lower surface of very large radius of curvature was placed on these screws so that a thin film of air lay between this surface of the lens and the upper polished surface of the slab. With the help of a mirror M and a right-angled prism P placed above the lens, horizontal rays of light from a sodium flame F were sent down vertically to illuminate the air film and the rays reflected repeatedly at the surface of the slab and the lower surface of the lens proceeded vertically upwards and were again reflected by the prism P and received by a horizontal telescope T so that Newton's rings could be seen through the telescope.

We know that in the case of Newton's rings the condition for a bright ring is

$$\delta = 2\mu e \cos r = (2n+1)\lambda/2,$$

where δ is the path difference, e the corresponding thickness of the air film and μ its refractive index, r the angle of refraction of the ray into the film, n the order of rings and λ the wavelength of the light used. In the present case $\mu = 1$, $r=0$. We have therefore

$$\delta = 2e = (2n+1)\lambda/2. \quad . \quad . \quad . \quad (4)$$

The difference in the thickness of the film at two successive bright rings is $\lambda/2$. Hence when the thickness of the film changes due to expansion of the slab and of the three screws supporting the lens the rings appear to pass across a mark in the lens. Since one-tenth of the distance between successive bright rings could be measured, the change in length of the order of $\lambda/2$ *i.e.* about 0·00002944 mm. could be determined.

When the above arrangement producing the air film was enclosed in a chamber which was heated, the thickness of the film changed due to the differential expansion of the screws and the substance B, and the shift of bright rings across the mark was observed. If x bright rings are thus shifted, the difference in the expansion of the projecting portion of the supporting screw and of the slab B along its thickness is equal to $x\lambda/2$. In order to find the expansion of the screws, the slab was removed and interference rings were produced by reflections at the lower surface of the lens and the polished surface of the metal plate through which the screws projected.

Abbe and Pulfrich improved Fizeau's apparatus by replacing the screws by quartz rings as shown in Fig. 5, p. 163. G and D are two quartz plates and R is a hollow cylindrical tripod, also of quartz, cut with its generating axis parallel to the optic axis, and placed between G and D. The specimen is placed inside R and the fringes are formed by the wedge-shaped air film enclosed between the lower surface of D and the upper surface of the specimen, the angle of the wedge being very small. The light from a Geissler tube (Fig. 6) containing mercury and hydrogen is used. It enters the telescope at right angles, is deviated through a right angle by means of the prisms P, P and then falls upon the system as a parallel beam. The fringe systems for different wavelengths are formed at different heights in the focal plane of the objective. By turning a screw any of these systems can be brought in the field of view of the micrometer eyepiece. The lower surface of the upper quartz plate D is provided with a mark of reference and the number of fringes crossing this reference mark due to rise of temperature can be measured with the help of the micrometer eyepiece. If λ_1, λ_2, λ_3.....denote the various wavelengths of light employed and $x_1+\xi_1$, $x_2+\xi_2$, $x_3+\xi_3$.....the number of interference bands displaced across a fixed line (x representing a whole number and ξ a fraction), the increase $\triangle$ in the thickness of the air film is given by

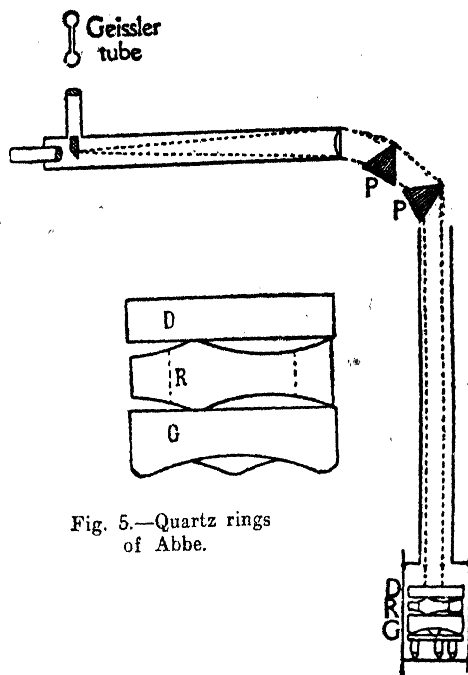


Fig. 5.—Quartz rings of Abbe.

Fig. 6.—Apparatus for measuring expansion of crystals by Fizeau's method.

$$\Delta = \frac{\lambda_1}{2}\left(x_1 + \xi_1\right) = \frac{\lambda_2}{2}\left(x_2 + \xi_2\right) = \frac{\lambda_3}{2}\left(x_3 + \xi_3\right) \quad . \quad (5)$$

9. The Fringe Width Dilatometer.—In the last method the change in length was found from observations on displacement of the fringes. Priest devised a dilatometer in which changes in length can be obtained from the change in width of the interference fringes. The apparatus is indicated in Fig. 7, p. 164.

The air film is enclosed between the lower surface of the cover plate and the upper surface of the base plate, both of which are optically plane and enclose a wedge-shaped space (0·1 to 0·3 mm. thick). The sample under test ends at the top in a fine point X upon which rests the cover plate. On looking down in the direction OO, a system of interference fringes will be seen (as shown in the plan) appearing to lie in the plane *bb* so that the fringes and the reference lines *ss* and *xx* on the mirror can be simultaneously focussed. When the sample expands on heating, it tilts the cover plate and thereby changes the thickness of the air film and consequently the *width* of the fringes. The number of fringes between the lines *ss* and *xx* are observed both initially and finally, and from this the expansion can be calculated.

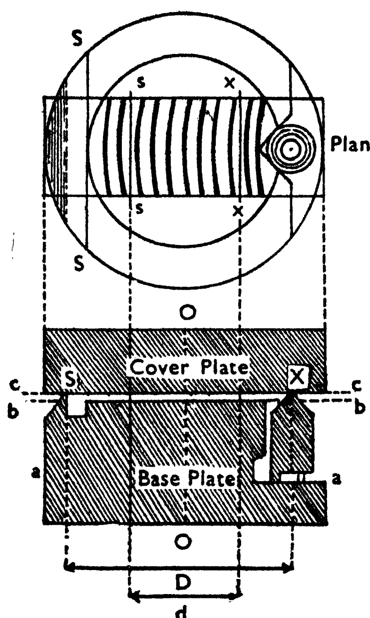


Fig. 7.—Fringe width dilatometer.

The calculations can be readily made. We saw from equation (4) in the last section that if the film thickness increases by $\lambda/2$, there is a shift of one fringe across the mark, the fringes actually contracting. Thus if in the present arrangement the number of fringes between the marks ss and xx changes by $x+\xi$, and d denotes the distance between ss and xx and λ the wavelength of the light employed, then the change ϕ in the angle between the planes bb and cc measured in radians is given by

$$\phi = (x+\xi)\frac{\lambda}{2}\cdot\frac{1}{d}. \qquad (6)$$

Again, if D is the perpendicular distance from X to knife-edge SS, $\triangle$ the relative expansion of the sample with respect to a piece of equal height made from the material composing the base plate, then ϕ is also given by

$$\phi = \frac{\triangle}{D}. \qquad (7)$$

Combining (6) and (7) we get

$$\triangle = \frac{\lambda D}{2d}(x+\xi). \qquad (8)$$

Knowing $\triangle$, the coefficient of expansion can be calculated.

10. Discussion of Results.— Table 1 gives the mean coefficient of expansion of several substances between 0 and 100°C. The mean coefficient λ multiplied by 10^6 is given in the table.

Table 1. Coefficient of Linear Expansion of Substances.

Substance	$\lambda \times 10^6$ per °C	Substance	$\lambda \times 10^6$ per °C
Aluminium ...	23·8	Platinum ...	8·86
Copper ...	16·66	Palladium ...	11·04
Cadmium ...	31·59	Silver ...	19·68
Chromium ...	8·4	Tungsten ...	4·5
Lead ...	28·0	Brass ...	18·9
Magnesium ...	26·0	Invar ...	0·9
Manganese ...	22·8	Jena glass ...	8·08
Molybdenum ...	5·20	Pyrex glass ...	3·3
Nickel ...	13·0	Quartz glass ...	0·510

But as already mentioned in section 3, these values change appreciably if the final temperature is different from 100°C. The mean coefficient λ is a function of the temperature. As the final temperature is lowered the coefficient decreases. Grüneisen has found the value of the quantity $\frac{1}{l_0}\frac{dl}{dt}$ for very low temperatures and has deduced an important law connecting the coefficient of expansion and the specific heat. Grüneisen's law states that *for a metal the ratio of the coefficient of linear expansion to its specific heat at constant pressure is constant at all temperatures.*

11. Surface and Volume Expansion.— The change in area and volume can be easily calculated from a knowledge of the coefficient of linear expansion. A rectangle of sides l and b will, on being heated, have sides of lengths $l(1+\lambda t)$ and $b(1+\lambda t)$, and its area will become $lb(1+\lambda t)^2$. If the initial and final areas be A_0 and A we have

$$A = A_0\,(1+2\lambda t)\text{ approx.}, \qquad (9)$$

since λ is small. Thus the coefficient of surface expansion is 2λ. Similarly, the coefficient of volume expansion can be shown to be 3λ

12. Expansion of Silica Glass, Invar.— Silica glass (quartz which has been fused and resolidified into the non-crystalline form) is now commonly employed for the construction of thermometers. The expansion of silica is very small ($\lambda = 0{\cdot}5\times10^{-6}$ per °C.), and is very conveniently determined by Fizeau's method. Vessels made of this material can be heated without any fear of breaking. The curve connecting the coefficient of expansion and temperature is a straight line between the room temperature and 1000°C. but at both limits it bends. The coefficient is negative below −80°C.

Invar is another special substance, being an alloy of nickel (36%) and steel. Its coefficient of expansion at ordinary temperatures is extremely small and hence it is generally employed for making secondary standards of length, and in the manufacture of precision clocks and watches.

Anisotropic bodies

13. It was first observed by Mitscherlich that the angles between the faces of cleavage of a crystal of Iceland spar change when the crystal is heated. He gave the correct explanation of the phenomenon, *viz.*, that the expansion of the crystal is different in different directions and this is the cause of the change in angle. Such substances are called anisotropic or non-isotropic.

For every crystal, however, there can be found three mutually perpendicular directions such that if a cube is cut out of the crystal with its sides parallel to these directions and heated, the angles will remain right angles though the sides will become unequal. These directions are called the *principal axes of dilatation* and the coefficients of expansion in those directions are called the *principal coefficients*

of expansion. Denote these by λ_x, λ_y, λ_z. Then a cube of sides l_0 will, on being heated to t°C, become a parallelopiped whose edges will be given by

$$l_x = l_0(1+\lambda_x t), \quad l_y = l_0(1+\lambda_y t), \quad l_z = l_0(1+\lambda_z t). \quad . \quad . \quad . \quad (10)$$

$$l_x\, l_y\, l_z = l_0^3[1+(\lambda_x+\lambda_y+\lambda_z)t]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The volume coefficient of expansion is thus $\lambda_x + \lambda_y + \lambda_z$ The linear expansion in any other direction can be readily calculated in terms of the principal coefficients and the direction cosines.*

14. Experimental Methods and Results.— Crystals are best investigated by the interference method. The crystal is cut in the manner desired, into a plate with parallel faces from 1 to 10 mm. thick, and is placed between the glass plate and the metal disc. The details of these experiments have already been given.

When the expansion along the various axes of different crystals is investigated very interesting results are obtained. In the hexagonal system, for optically negative crystals the expansion along the axis is always greater than that along an axis at right angles to it ; while for optically positive crystals the reverse is the case. Thus, for Iceland spar we have expansion parallel to the axis and contraction perpendicular to it. The contraction is always much less than the expansion so that the volume coefficient remains positive.

EXPANSION OF LIQUIDS

15. In case of liquids we have to consider only the cubical expansion. As before, the volume can again be expressed as a function of the temperature ; thus

$$V = V_0(1+\alpha_1 t+\alpha_2 t^2+ \quad . \quad . \quad), \quad . \quad . \quad . \quad . \quad (12)$$

or approximately,

$$V = V_0(1+\alpha t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where α is called the mean coefficient of expansion between 0° and t°C. Thus if a mass M of the liquid occupies the volumes V, V_0 at t° and 0°C, the densities ρ, ρ_0 of the liquid at the respective temperatures are $\rho = M/V$, $\rho_0 = M/V_0$. Using (13) we get the relation

$$\frac{\rho_0}{\rho} = \frac{V}{V_0} = 1+\alpha t. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The expansion of liquids is much greater than that of solids, yet it is more difficult to measure, for it is complicated by the expansion of the containing vessel. The expansion observed is called the apparent expansion and is a combination of the two effects, *viz.*, expansion of the liquid and of the containing vessel. It can be shown (see sec. 17) that the coefficient of absolute expansion of the liquid is approximately equal to the sum of the coefficients of expansion of the containing vessel and the coefficient of apparent expansion of the liquid. Thus the former can be determined if the latter two quantities are known.

* Further see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p. 876.

There are three well known methods for determining the apparent or relative expansion :—

(*i*) The Volume Thermometer Method, (*ii*) the Weight Thermometer Method, and (*iii*) the Hydrostatic Method.

16. The Dilatometer or Volume Thermometer Method.— The thermometer consists of a bulb to which a graduated stem is attached. It is nearly filled with the liquid to be experimented upon. If the liquid stands to the mark x_0 on the stem at 0°C., and to the mark x_1 at t°C., and if the volume of the bulb at 0°C. is V_0 and of each division of the stem v_0, then the volumes of the liquid at the two temperatures are

$$V_0+x_0v_0 \text{ and } (V_0+x_1v_0)(1+\gamma t),$$

γ being the expansion of the containing vessel. The volume at t°C. is also equal to

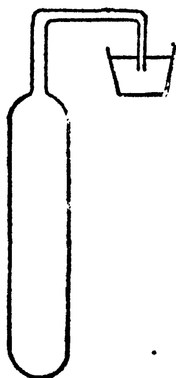
$$(V_0+x_0v_0)(1+\alpha t),$$

where α is the coefficient of absolute expansion of the liquid. Equating we have

$$(V_0+x_0v_0)(1+\alpha t) = (V_0+x_1v_0)(1+\gamma t)$$

Knowing γ the true coefficient α is calculated, or if γ is not known, the relative expansion $\alpha-\gamma$ can be evaluated.

17. The Weight Thermometer Method.— A more accurate method, depending upon the determination of weight and not of volume is furnished by the pyknometer or the weight thermometer. These are vessels so constructed as to take a definite volume of the liquid. The weight thermometer is of the shape shown in Fig. 8, and is made of glass or fused silica. It is first weighed and then completely filled with the liquid by alternate heating and cooling with the open end dipping in a cup of the liquid.


Fig. 8—The Weight Thermometer.

The experiment consists in weighing the thermometer filled with the liquid at two temperatures. Let w_1, w_2 represent the weights of the liquid filling the thermometer at temperatures t_1 and t_2 respectively. If V_1, V_2 are the volumes of the vessel at the two temperatures and ρ_1, ρ_2 the corresponding densities of the liquid, then

$$w_1 = V_1\rho_1, \quad w_2 = V_2\rho_2. \quad . \quad (15)$$

But if α, γ denote the expansion coefficient of the liquid and the vessel respectively,

$$\frac{V_2}{V_1} = \frac{1+\gamma t_2}{1+\gamma t_1}; \quad \frac{\rho_2}{\rho_1} = \frac{1+\alpha t_1}{1+\alpha t_2}$$

$$\therefore \quad \frac{w_1}{w_2} = \frac{1+\gamma t_1}{1+\gamma t_2} \cdot \frac{1+\alpha t_2}{1+\alpha t_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$= 1+(\alpha-\gamma)(t_2-t_1) \text{ approx.} \quad . \quad . \quad . \quad . \quad (17)$$

The apparent expansion a can be obtained from (16) or (17) if

the expansion of glass is disregarded i.e., γ is put zero. We then obtain from (17)

$$\frac{w_1}{w_2} = 1 + a(t_2 - t_1) \text{ approx.}$$

or
$$a = \frac{w_1 - w_2}{w_2(t_2 - t_1)} \text{ approx.} \qquad \ldots\ldots \quad (18)$$

Equation (16) can be treated rigorously. Assuming t_2 to refer to 0 °C, and dropping the suffix 1, equation (16) yieds

$$\frac{w}{w_0} = \frac{1+\gamma t}{1+\alpha t},$$

or
$$\alpha = \frac{w_0 - w}{wt} + \frac{w_0}{w}\gamma. \qquad \ldots\ldots \quad (19)$$

$$= a + \frac{w_0}{w}\gamma \qquad \ldots\ldots \quad (20)$$

It is thus seen that, rigorously speaking, the true expansion coefficient is a little more than the sum of the apparent coefficient and the expansion coefficient of glass, though the difference is almost negligible, and for all practical purposes we can assume $\alpha = a + \gamma$. We could treat equation (16) more generally when the result will be more complicated than (20). Knowing γ the absolute expansion α can be calculated.

The thermometer can also be employed to find the cubical expansion of solids indirectly by enclosing the specimen inside the thermometer.*

18. Hydrostatic Method (Matthiessen's method).—This consists in finding the apparent weight of a solid when immersed in the liquid at two temperatures t_1, t_2 respectively. The loss in weight of the solid is by Archimedes' principle equal to the weight of a volume of the liquid equal to that of the solid ; denote this quantity by w. Then

$$w_1 = V_1\rho_1, \quad w_2 = V_2\rho_2,$$

where V_1, V_2 denote the volumes of the solid at the two temperatures t_1, t_2 respectively. Then

$$\frac{V_1}{V_2} = \frac{1+\gamma t_1}{1+\gamma t_2}, \qquad \frac{\rho_1}{\rho_2} = \frac{1+\alpha t_2}{1+\alpha t_1},$$

and proceeding as before,

$$\alpha - \gamma = \frac{w_1 - w_2}{w_2(t_2 - t_1)} \text{ approx.} \qquad \ldots \quad (21)$$

An equation analogous to (19) can also be deduced.

19. Absolute Expansion of Liquids.—As already mentioned, the three foregoing methods may be employed to find the absolute expansion of a liquid provided the cubical expansion of the containing vessel [or of the immersed solid in § 18] be known. One way

* See Glazebrook, *A Dictionary of Applied Physics*, Vol. 1 p. 878.

of finding the latter is by calculating it from the linear expansion. This is, however, open to objection for the linear expansion is determined from bars of the material and it cannot be assumed *a priori* that the physical properties of the material do not change when it is annealed and worked into a vessel of some shape. For this reason it is best to select vessels of fused silica for which the volume coefficient is extremely small (about 0·0000015 per °C.)

20. Hydrostatic Balance Method.— There is only one direct method of determining the absolute expansion of a liquid which was first given by Dulong and Petit. It depends on the hydrostatic balancing of two liquid columns at different temperatures. Dulong and Petit employed a simple U-tube for the purpose. Regnault brought the upper ends of the tube close together, an improvement which made it easier to observe the difference in height of the two columns. The diagram (Fig. 9) serves to illustrate the principle of the method. A glass or metal tube, bent as shown in the figure, contains mercury. The vertical columns AB, CD, C′D′ are surrounded by melting ice and are thereby maintained at 0°C., while the column A′B′ is surrounded by an oil bath maintained at any temperature t°C. Suppose that AA′ is horizontal. Let H, H', h, h' denote the heights of mercury in the various columns as shown and ρ, ρ_0 the densities of mercury at t°C. and 0°C. Then since the pressures at D and D′ are equal, we have by equating the two expressions for the hydrostatic pressure at A,

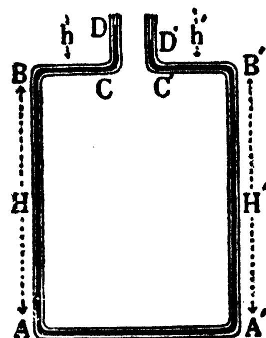


Fig. 9.—Hydrostatic Balance Method.

$$h'\rho_0 + H'\rho = H\rho_0 + h\rho_0 . \qquad (22)$$

But

$$\rho = \rho_0/(1+ct),$$

where c is the coefficient of absolute expansion of mercury. Hence

$$\frac{H'}{1+ct} + h' = H + h, \qquad (23)$$

whence c can be calculated.

If the columns H, h, h' are not at 0°C. but at temperatures t_1, t_2, t_3 respectively we shall get

$$\frac{H'}{1+ct} + \frac{h'}{1+c_3t_3} = \frac{H}{1+c_1t_1} + \frac{h}{1+c_2t_2} \qquad (24)$$

where the quantities c_1, c_2, c_3 denote the mean coefficients of expansion between the different ranges. These can be determined by having the temperature of A′B′ to be t_1, t_2, t_3 successively. If the height of A′ above A is h_1, a corresponding term can be added to the right-hand side.

Regnault's observations, though carried out with great skill, must be corrected for various sources of error and hence cannot yield

results of high accuracy. Callendar and Moss repeated the experiments aiming at a high degree of accuracy. Instead of a single pair of hot and cold columns 1·5 m. long employed by Regnault, they used six pairs of hot and cold columns each 2 m. long and connected in series as shown diagrammatically in Fig. 10. The hot and cold columns are marked H and C respectively. The difference in height of the first and the last column (*viz.*, *ab*) is six times that due to a single pair.

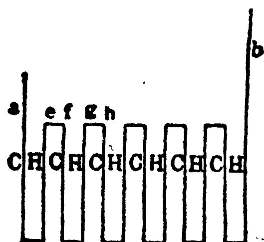


Fig. 10.—Arrangement of Callendar and Moss's apparatus.

In the actual apparatus *ef*, *gh* . . . were doubled back so that all the columns marked C were one behind the other, and similar was the case with H columns. All the H columns were placed in one limb of a rectangle and all the C columns in one limb of another rectangle, while the other limbs of these rectangles contained electrically heated oil and ice-cooled baths respectively. These were kept circulating by means of an electric motor and their temperatures were determined by a long 'bulb' resistance thermometer. Experiments were performed in the range 0 to 300°C. and an accuracy of 1 in 10,000 was aimed at.

21. Results for Mercury.— Their values for mercury are, however, systematically different from the mean of earlier investigators such as Regnault and Chappuis. Harlow has also made accurate determinations with the help of a weight thermometer of silica and aimed at an accuracy of 1 in 18,000. The concordance of results with bulbs of different shapes showed that silica was quite isotropic. The coefficient of expansion in the region 0 to 100°C. is according to Callendar and Moss 0·000182 per °C.

The following numerical examples show how the expansion of mercury is taken into account in (a) *the correction of the barometric reading for temperature*, (b) *the correction for the emergent column of a mercury thermometer* and (c) *the compensation of the mercury pendulum*.

Example 1.—A barometer having a steel scale reads 750·0 mm. on a day when the temperature is 20°C. If the scale is correctly graduated at 0°C., find the true pressure, given that the coefficient of linear expansion of steel $= 12\times10^{-6}$ $°C^{-1}$, and coefficient of expansion (absolute) of mercury $= 182\times10^{-6}$ per °C.

The length of scale at 20°C. $= 75{\cdot}00\ (1+20\times12\times10^{-6})$ cm.

Density of mercury at 20°C. $= \rho_0/(1+20\times182\times10^{-6})$

where ρ_0 is density of mercury at 0°C.

$$\therefore\ \text{Pressure} = \frac{75{\cdot}00(1+20\times12\times10^{-6})\,\rho_0 g}{(1+20\times182\times10^{-6})}\ \text{dynes/cm}^2.$$

$$=75{\cdot}00(1-0{\cdot}0034)\ \rho_0 g = 74{\cdot}745\ \rho_0 g\ \text{dynes/cm.}^2$$

Example 2.—A mercury thermometer, immersed up to 30°C. mark in a hot liquid reads 230°C. If the exposed stem has an average temperature of 50°C., calculate the true temperature, given that mean coefficient of expansion of mercury is 182×10^{-6} per °C, and coefficient of linear expansion of glass $= 8 \times 10^{-6}$ °C^{-1}.

Coefficient of apparent expansion of mercury

$$= (182 - 3 \times 8)10^{-6} = 158 \times 10^{-6} \text{ °C}^{-1}.$$

Hence, the exposed stem, if at the true temperature t°C., would occupy a length $(230-30)$ $[1+(t-50)\ 158 \times 10^{-6}]$.

$$\therefore \quad t - 230 = (230-30)(t-50)158 \times 10^{-6},$$

whence $t = 235$°C.

Example 3.—In a mercury pendulum a steel rod of length l cm. at 0°C supports a glass cistern containing mercury. Find the height to which mercury should be filled up in the cistern for perfect compensation of the pendulum, given that the linear coefficient of expansion of steel $\alpha = 12 \times 10^{-6}$, linear coefficient of expansion of glass $g = 8{\cdot}5 \times 10^{-6}$, cubical coefficient of expansion of mercury $m = 1{\cdot}82 \times 10^{-4}$ °C^{-1}.

Let h be the required height of mercury in the cistern at 0°C, V the volume of that mercury and A the cross-sectional area of the cistern, both at 0°C. Due to the rise of temperature to t°C, the volume of mercury increases to $V(1+mt)$, the cross-sectional area of the cistern increases to $A(1+2gt)$ and therefore the height of mercury increases to

$$\frac{V(1+mt)}{A(1+2gt)} = h(1+mt-2gt).$$

Since the centre of gravity of mercury at 0°C is at a height $h/2$ from the bottom, it will rise to $(h/2)(1+mt-2gt)$ at t°C, the increase being $(h/2)(mt-2gt)$. The increase in the length of the steel rod at t°C is $l\alpha t$. For perfect compensation these two changes must be equal. Hence

$$\frac{h}{2}(mt-2gt) = l\,\alpha\,t.$$

Or $$h = \frac{2\alpha}{m-2g}\,l = \frac{2 \times 12 \times 10^{-6}}{(182-17) \times 10^{-6}}\,l = 0{\cdot}145\,l.$$

22. Expansion of Water.— It is well-known that the expansion of water is anomalous in the region 0 to 4°C. Several workers such as Hope, Despretz, Matthiessen, Joule and Playfair and others, measured this expansion carefully. A constant volume dilatometer (sec. 16) may be employed for this purpose. If the dilatometer is made of ordinary glass some mercury is initially put in it to compensate for the expansion of glass. Since the expansion of mercury is 0·000182 and of glass 0·0000255, a volume of mercury equal to one-seventh of the volume of the dilatometer will be required for compensation. These experiments show that when water at 0°C is heated it goes on contracting as long as the temperature is below 4°C. Above 4°C it

expands on heating. Accurate experiments by Joule and Playfair show that this temperature of maximum density is 3·95°C. This anomalous behaviour is usually explained on the assumption that there exist three types of molecules H_2O, $(H_2O)_2$ $(H_2O)_3$, which have different specific volumes and are mixed in different proportions at different temperatures. The total volume occupied is assumed to be the sum of the specific volumes, though there seems to be little justification for such an assumption.

PRACTICAL APPLICATIONS OF EXPANSION

23. The expansion of solids and liquids is of great importance in our daily life and its consequences have often to be borne in mind carefully. The student will be familiar with most of these from his elementary studies. Thus it is well-known that allowance must be made for expansion in the laying of railway lines and the erecting of steel bridges, the contraction of metal tyres on cartwheels etc. The expansion of the steel scale must be taken into account in reading the barometer (sec. 21, Example 1). Similarly the expansion of mercury must be found out for obtaining the true temperature from a mercury thermometer (sec. 21, Example 2). Expansion in optical and electrical apparatus also causes difficulties. The mirrors of reflecting telescopes which are very accurately figured must be protected from distortion of their surface by expansion of different portions which may be at different temperatures. The inductance of a coil depends upon its dimensions and therefore changes with expansion of the coil.

In dealing with glassware it is particularly important to remember the consequences of expansion and contraction as the glass is likely to break when subjected to sudden changes of temperature. This is because glass is a poor conductor of heat and the difference in temperature between the different parts causes unequal expansion. Breakage is avoided by either choosing thin glassware or choosing glass of small coefficient of expansion and high thermal conductivity. Fused silica vessels can be heated to white heat and plunged safely into cold water, while pyrex glass can be thrust into a blowpipe flame suddenly without risk of fracture. Platinum wires can be sealed into ordinary glass (lead glass) without any risk of a crack developing because platinum and glass have practically the same coefficient of expansion but a copper wire would cause cracks to develop due to unequal expansion.

24. Compensation of Clocks and Watches.—For our present purpose the pendulum of a clock may be treated as a "simple pendulum" with a bob of negligible dimensions suspended at the end of a wire of negligible mass. The time kept by the clock depends upon the time of oscillation of its pendulum which, in the case of a simple pendulum, varies as the square root of the length of the pendulum. The length of the simple pendulum is the distance between the point of support and the centre of gravity of the bob. Thus if this length

increases in summer due to expansion, the time of oscillation will increase and the clock will lose time. If the length decreases due to fall of temperature, the pendulum swings faster and the clock gains. Therefore unless the pendulum is compensated against the effect of expansion the clock will gain in winter and lose in summer. This compensation is brought about by the use of two expansible materials so arranged that the expansion of one is compensated by the expansion of the other.

In the *gridiron pendulum* alternate rods of steel and brass are connected as shown in Fig. 11 so that the steel rods expand only downwards, and the brass rods only upwards. It is so arranged that $l_1 \alpha_1 = l_2 \alpha_2$ where l_1 and l_2 are the total lengths of the steel and brass rods respectively, and α_1, α_2 the respective coefficients of linear expansion. Under these conditions the effective length of the pendulum remains constant at all temperatures and the pendulum is compensated. It will be seen that $l_1/l_2 = \alpha_2/\alpha_1 = 3/2$ approximately.

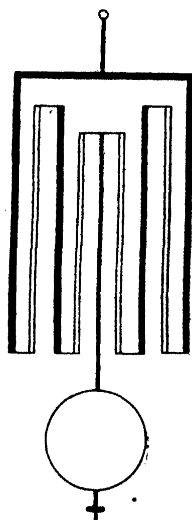


Fig. 11.—Gridiron pendulum.

In the mercury pendulum a long steel rod carries, in place of the ordinary bob, a frame fitted with two glass cylinders containing mercury. Compensation is obtained by the expansion of the rod downwards and the expansion of mercury upwards. (See sec. 21, Example 3).

In *watches* the rate of movement is governed by the oscillation of a small flywheel called the balance wheel which is itself controlled by a hairspring. The time of oscillation of the balance wheel depends upon the stiffness of the hair-spring and the moment of inertia of the wheel about its axis of oscillation. The moment of inertia depends on the diameter of the wheel and is mainly contributed by the three small weights (Fig. 12) screwed on the rim of the wheel. A rise in temperature weakens the hair-spring and increases the diameter of the balance wheel. Both these changes cause the oscillations to become slower, the former effect being more important. To effect compensation, the rim of the balance wheel is made in three segments of a bimetallic strip with brass on the outside and steel on the inside, and weighting the rim with three weights as shown in the figure. Due to the larger expansion of brass the end of each segment curls inwards when the temperature rises thereby reducing the moment of inertia sufficiently to compensate both for radial expansion and weakening of the hair-spring. The precision watches such as chronometers are usually provided with compensated balance wheels. Inver steel is now frequently used in the manufacture

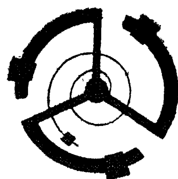


Fig. 12.—Compensated balance-wheel.

of pendulums and balance wheels on account of its very small coefficient of expansion.

25. Thermostats.— The property of expansion is often utilised for constructing thermostats. In these the temperature of any substance can be kept constant for a long time. For temperatures upto 100°C, a toluene thermostat may be used but for temperatures above 100°C, a bimetallic thermo-regulator is generally used. These will now be described.

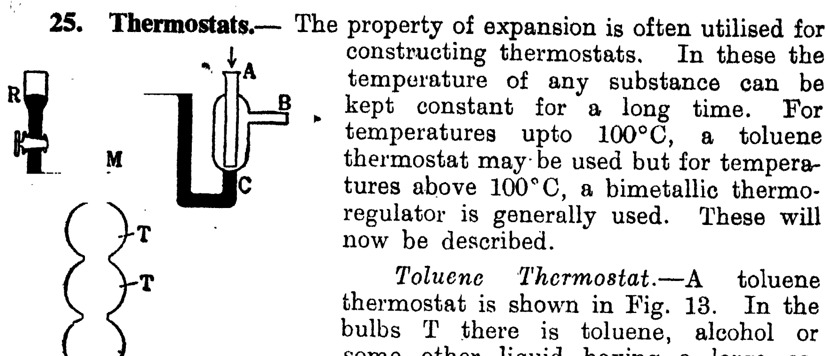


Fig. 13.—Toluene Thermostat.

Toluene Thermostat.—A toluene thermostat is shown in Fig. 13. In the bulbs T there is toluene, alcohol or some other liquid having a large coefficient of expansion. These bulbs are immersed in the bath whose temperature is required to be maintained constant. In case the temperature of the bath increases the toluene expands and forces the mercury (shown black in the figure) up the tube in C and thereby closes the opening leading from A to B. The bath is heated by a burner and the gas feeding this burner is supplied through A and this opening. Thus, on account of the expansion the gas supply is decreased and the temperature falls. If the temperature of the bath falls too much, toluene contracts, the opening is increased and gas supply increases. By adjusting the amount of mercury in R the temperature can be kept constant at any desired value. In case of electrical heating suitable electrical contact can be arranged above the mercury level for switching off the heating current.

Bimetallic Thermo-Regulator—The Dekhotinsky bimetallic thermo-regulator is shown in Fig. 14. It consists of a compound strip R, which is made by welding together brass and invar steel. The strip is wound into a small helix and is connected by means of the rod P to the contact maker C which makes or breaks the electrical circuit of the heater H. When the temperature rises the expansion of the brass causes the helix to unwind and thereby the contact at C is opened thus breaking the electrical circuit. With fall in temperature the helix contracts and thus contact is made at C thereby completing the electrical circuit. With this apparatus temperatures up to 300°C. can be maintained to within ±1°C. for a long time.

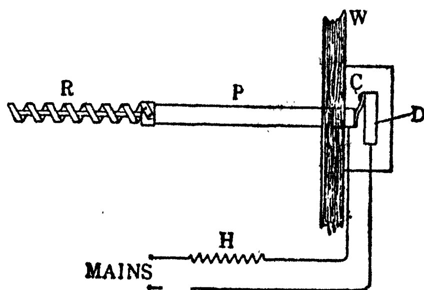


Fig. 14.—The Bimetallic Thermo-Regulator.

EXPANSION OF GASES

26. Expansion of Gases.— The expansion of gases forms the very basis of the system of thermometry and the perfect gas scale discussed in Chap. I. As stated there the results are best expressed in the form of Charles' law which holds very approximately for the so-called permanent gases in nature. Here we shall describe the experimental methods of determining the coefficient of expansion.

In the case of gases it is necessary to distinguish between two coefficients of expansion: (1) the volume coefficient of expansion α at constant pressure, and (2) the pressure coefficient of expansion β at constant volume. The volume coefficient of expansion is defined as the increase in volume of unit volume at 0°C for each centigrade degree rise of temperature at constant pressure. Thus

$$\alpha = \frac{V - V_0}{V_0 t} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where V and V_0 denote the volumes of a fixed mass of gas at $t°$ and 0°C. Or

$$V = V_0(1+\alpha t). \quad . \quad . \quad . \quad . \quad . \quad (26)$$

If the volumes at temperatures t_1 and t_2 are V_1 and V_2 respectively, we get, with the help of (26),

$$\alpha = \frac{V_2 - V_1}{V_1 t_2 - V_2 t_1} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

We can thus determine α by measuring the volume of a fixed mass of gas at two temperatures.

Similarly the pressure coefficient of expansion of a gas is defined as the increase in pressure, expressed as a fraction of the pressure at 0°C. for one centigrade degree rise of temperature when a fixed mass of the gas is heated at constant volume. Thus if p and p_0 be the pressures at $t°$ and 0°C we have

$$\beta = \frac{p - p_0}{p_0 t} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

from which relations analogous to (26) and (27) can be deduced.

27. Experimental determination of the Volume Coefficient of Expansion.— Gay-Lussac was among the earliest to measure the volume coefficient accurately. Regnault used an improved form of apparatus and corrected his results for various sources of error. Fig. 11 shows a laboratory arrangement for determining the volume coefficient and employs Regnault's technique in a simplified form.

The bulb A is connected by a narrow glass tube to a calibrated limb B of a mercury manometer whose other limb C can be moved up and down for adjusting the mercury level in B. The tap T enables the quantity of gas in A to be adjusted. First the bulb A is put in a cold water bath at $t_1°$, and after it has acquired the temperature of the bath, the tube C is adjusted until the mercury stands at the same level in both arms, and the mercury level in B noted. Then the

bath is heated, when the enclosed air expands pushing the mercury down in B and up in C. The bath is maintained at a certain temperature and the tube C lowered to bring the mercury level at the same height in B and C, and the volume of gas in B read from the graduations. The process is repeated for every 20° rise of temperature upto 100°C, and the observed readings are utilised for calculating α from (27).

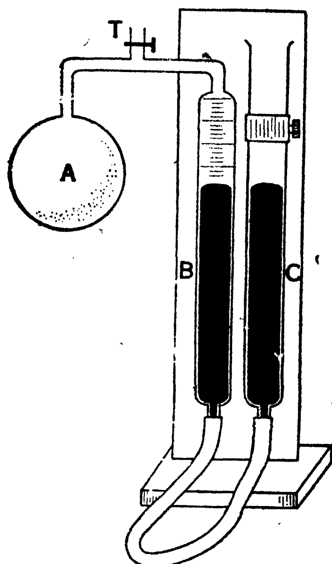


Fig. 15.—Apparatus for measuring volume coefficient.

The results are best treated by plotting the observed volumes against temperature on a graph. It is found that all the points lie on a straight line showing that equal changes in temperature lead to equal changes in volume at constant pressure. This is Charles' law which may be formally stated: *for a fixed mass of gas heated at constant pressure, the volume increases by a constant fraction of the volume at 0°C for each centigrade degree rise in temperature.* This also follows from the result that α comes out to be the same whatever values of t_1 and t_2 are utilised in (27). Results further show that $\alpha = 1/273$ (nearly) for all the so-called **permanent gases.**

For accurate work corrections must be applied for the following sources of error:—(1) the gas in the narrow tube and the manometer is at a different temperature from the bath, (2) the expansion of the glass bulb with rise of temperature. Regnault applied corrections for these and found that all *real* gases showed small departures from uniform expansion and that the coefficient of expansion differed slightly from one gas to another.

28. Experimental determination of the Pressure Coefficient of Expansion.— The pressure coefficient can be easily determined in the laboratory with the help of an apparatus known as Joly's apparatus. It consists of a glass bulb A, of about 100 c.c. capacity, which is filled with dry air and is connected by a glass

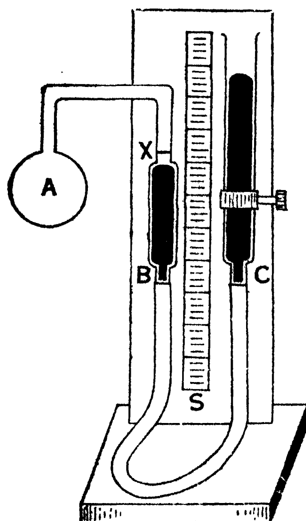


Fig. 16.—Joly's apparatus for determining pressure coefficient.

capillary tube to a mercury manometer mounted on a stand (Fig. 16). A fixed reference mark × is made on the tube B near the top by means of a file, and the mercury level is always brought to this mark by adjusting C before any reading is taken. This ensures that the volume of the enclosed gas is kept constant. A metre scale S is fixed to the vertical stand to read the difference h in the levels of mercury in the two tubes B and C. The bulb A is immersed in a water bath which is well stirred, and temperatures are read with a mercury thermometer.

First the experiment is done with cold water in the bath and the difference h in the levels of mercury in the two columns noted. If the barometric height is H, the pressure of the gas is $H \pm h$ depending upon whether the level in C is higher or lower than that in B. The bath is then heated through about 20°, heating stopped, and the bath well stirred. The mercury is again brought to the reference mark and the level watched carefully. When the level becomes steady at the reference mark, the reading in C is noted. Heating is then resumed and readings are taken in this way at intervals of 20°. The coefficient of expansion β is then calculated from the relation

$$\beta = \frac{p_2 - p_1}{p_1 t_2 - p_2 t_1} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

For accurate work various corrections are necessary. The most difficult to estimate is the "dead space" correction (p. 9) since the exact temperature of the gas in the capillary tube is not known. The expansion of the bulb introduces an error in β of the order of 1% ; this can be satisfactorily corrected for by adding the coefficient of cubical expansion of glass to the observed value of β. Experiments have shown that β is fairly close to 1/273 for all the permanent gases which means that for a fixed mass of any gas heated at constant volume, the pressure increases by 1/273 of the pressure at 0°C for each centigrade degree rise in temperature. Accurate experiments however show that this expansion is neither uniform for a gas, nor is it exactly the same for all gases.

As mentioned in §7, Chap. I, these observed deviations of α and β from the correct value of 1/273·16 are really due to the deviations of actual gases from Boyle's law. Let a fixed mass of perfect gas, which by definition obeys Boyle's law, have the pressure p_0 and volume v_0 at 0°C. When it is heated to t°C, the product of pressure and volume can be written as $p_0 v_0(1+\alpha t)$ or $p_0 v_0(1+\beta t)$ depending on whether the pressure is kept constant or the volume is kept constant. Since these products must be equal by Boyle's law, we get $\alpha = \beta$ for a perfect gas. The expansion coefficient is experimentally found to be 0·0036608 for all gases provided they are reduced to the state of a perfect gas ($p \longrightarrow 0$). The equality of α for all gases is really a consequence of the kinetic theory.

Book Recommended

1. Glazebrook: *A Dictionary of Applied Physics*, Vol. I, pp. 872—900.

CHAPTER VIII

CONDUCTION OF HEAT

1. Methods of Heat Propagation.— When a bar of metal is heated at one end and held at the other by the hand we feel the sensation of heat. Heat travels from the hot end along the bar and produces this sensation in the hand. The power of transmitting heat in this manner is possessed by all substances to a varying degree and this phenomenon is called *Conduction of Heat.*. In the process of *Convection*, heat is transferred by the actual motion of heated particles of matter whether liquid or gaseous. This is best illustrated by placing gently some crystals of potassium permanganate at the bottom of a beaker containing water and heating it. Heated water rises up and curls down forming a closed path which is rendered visible by the red colour imparted to the water. In conduction, heat is transferred by 'contact' and there is no apparent transfer of matter.

In both the above processes the intervening medium takes an active part in heat propagation, but in addition to these there is another process in which the intervening medium takes no part. If we stand near a coal furnace, we feel the sensation of heat. If we are in the sun, we feel warm. Here the source of heat is the coal-furnace or the sun, and in the latter case it is at an enormous distance from us. There is absolutely no material medium between us and the sun, still heat from the sun continues to reach us. This phenomenon is called *Radiation.* The processes of conduction and convection are necessarily slow due to the action of the intervening medium while radiation travels with the enormous velocity of light. In this chapter we shall consider the conduction of heat.

2. Conductivity of Different Kinds of Matter.—Common observations show that different substances vary enormously in their conducting power. A glass rod can be melted in a flame by holding it at a point two or three inches away from the flame, while a copper rod under similar conditions becomes too hot to touch. Copper is thus a better conductor of heat than glass. Metals, in general, are good conductors of heat; glass, wood and other non-metals are bad conductors. Hold inside a flame two blocks, one of wood and the other of copper, each covered with paper. The paper covering the copper block is not burnt, for heat is rapidly conducted away by copper and the temperature does not rise to the ignition point. The paper covering the wood is burnt. Similarly, water may be boiled in a cup of paper for the heat is taken up by water (convection).

Liquids, in general, are worse conductors of heat than solids and gases are the worst. A very simple experiment shows that water is a very bad conductor of heat. Take some water in a test-tube and sink into it a piece of ice by weighting it. The water at the top can be boiled by heating it locally while the ice at the bottom does not even

melt. Air and gases, in general, are even worse conductors than water. Woollen clothing protects us from cold on account of the fact that it contains air in the interstices which renders it a very bad conductor of heat.

The good conductivity of metals is utilised in the construction of the Davy safety lamp. The flame is enclosed in an iron gauze chamber (Fig. 1) and can be taken down a mine. Any combustible gas, if present, comes in contact with the naked flame and burns inside the chamber. But the iron gauze conducts away heat so quickly that the temperature at any point of it does not rise to the ignition point and the outer gas does not ignite.

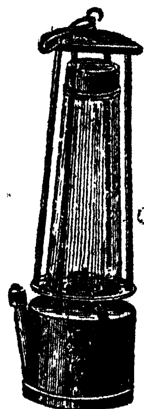


Fig. 1.—Davy Safety Lamp.

3. Definition of Conductivity.— The first to give a precise definition of conductivity was Fourier who in his memorable *Theorie Analytique de la Chaleur* (1822) treated the subject of heat conduction in a masterly way and placed it on firm mathematical basis. We shall first discuss the flow of heat inside a bar heated at one end. Consider a thin wall of the material with parallel faces such that heat flows in a direction perpendicular to the faces. Let θ_1, θ_2 be the temperatures of the two faces, l the thickness of the wall, A the area of each face, then it can be shown experimentally that the amount of heat Q flowing through the wall in a time t, when the temperature at every point of the bar is steady, is directly proportional to (*i*) $\theta_1 - \theta_2$, (*ii*) the area A of the surface, (*iii*) the time t and (*iv*) inversely proportional to l, that is,

$$Q = KA \frac{\theta_1 - \theta_2}{l} t. \qquad (1)$$

The coefficient K is a quantity depending upon the nature of the substance and is called its *thermal conductivity*. From this relation conductivity may be defined as *the quantity of heat flowing per second through a unit area of plate of unit thickness, when the difference of temperature between the faces is unity.* In analogy with the electrical resistance, the inverse of K may be called the *thermal resistance* of a unit cube.

Now imagine the thickness of the plate to be diminished indefinitely. The limiting value of $\frac{\theta_1 - \theta_2}{l}$ or $-\frac{\theta_2 - \theta_1}{l}$ is $-\frac{d\theta}{dx}$ and denotes the temperature gradient at any point. The minus sign has been used before $\frac{d\theta}{dx}$ because the symbol d always stands for the increase. Hence, the quantity of heat Q flowing in the positive direction of x in time dt across the isothermal surface of area A at any point x is given by

$$Q = -KA \frac{d\theta}{dx} dt. \qquad (2)$$

This equation is of fundamental importance in the theory of heat conduction. The units in which conductivity is measured in the C.G.S. system are the calorie per second per square centimetre of area for a temperature gradient of 1°C. per cm. [cal. cm.$^{-1}$ sec^{-1} °C^{-1}].

CONDUCTIVITY OF METALS

4. We shall now give the various methods of determining the thermal conductivity of metals. Methods I to III employ stationary heat-flow while in IV a stationary periodic flow of heat is used.

I. Conductivity from Calorimetric Measurement

5. The definition of conductivity from equation (1) provides a simple method of determining the conductivity of a substance. We need have only a slab of the material of known cross-section heated at one end, and measure the amount of heat that flows out at the other end in a known time, as well as the temperature of the two faces. Thus all the other quantities except K in equation (1) are known, and hence K can be evaluated.

The method though simple presents considerable experimental difficulties. It is difficult to measure accurately the temperature of the two faces of a slab of metal. This is best achieved by keeping embedded in the surface the junction of a thermocouple, the use of mercury thermometer or resistance thermometer being inconvenient or impossible. Some early experimenters used steam to heat the slab at one end and ice or water to cool it at the other end, and assumed that the temperature of the end faces of the slab was that of steam and water respectively. But if proper precautions be not taken, the method sometimes gives absurd results. This is on account of the fact that a thin film of fluid always at rest, is formed in contact with the surface, and this has a large temperature gradient. Hence it is essential that we should observe the temperature inside the slab itself by means of thermometers. There are many apparatus based on this method, and one due to Searle is described below.

Fig. 2 shows the apparatus diagrammatically. One end B of the rod AB is enclosed in the steam-chamber S while the other end A projects into another chamber C through which cold water circulates as indicated, the temperatures at entry and exit being T_3 and T_4 respectively. Temperatures at two points along the bar are measured by thermometers T_1 and T_2; let these be T_1 and T_2. The whole rod is wrapped round with some non-conducting material like wood, felt, etc. In the steady state if m grams of water flow past the cold end of the bar per second, the heat conducted by the bar per second is $m(T_4-T_3)$ and this equals $AK\dfrac{T_1-T_2}{d}$, where d is the distance between the thermometers T_1, T_2. Thus, the conductivity K is determined.

In the foregoing experiment some heat was lost by radiation from the sides of the bar. This is a source of error and is very

easily eliminated if the bar be surrounded with some material at the same temperature as the adjacent portions of the bar. There will be no flow of heat perpendicular to the length of the bar as no

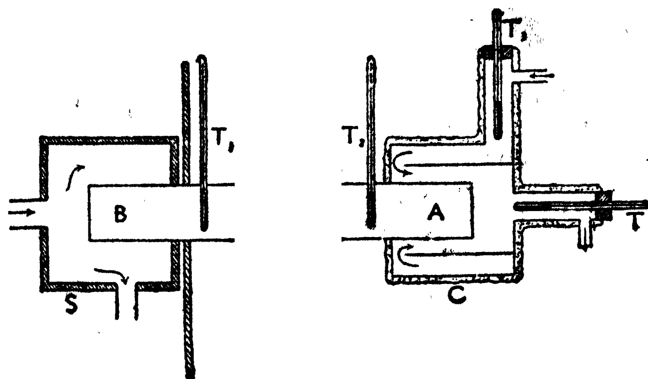


Fig. 2.—Searle's apparatus.

temperature gradient exists in that direction. The surrounding material is called the 'guard-ring'.

Berget utilised this guard-ring method for determining the conductivity of various substances such as copper, iron, brass and mercury. A vertical cylindrical column of mercury is surrounded by an annular ring of mercury. In both the upper surface of mercury is heated by steam while the lower surface rests on a metal plate cooled by ice. Thus the temperature gradient as well as the temperatures at the same level in the experimental column and the surrounding annular ring are identical. Under these conditions there can be no lateral flow of heat and the annular ring serves as a 'guard-ring'. The lower end of the experimental column projects into the bulb of a Bunsen ice-calorimeter and the heat flowing out at the lower end is found from the indications of the mercury thread. The difference of temperature between several points along the column is determined by four differential thermo-couples. The conductivity K can be calculated from formula (1).

This method has been adopted by a number of workers, notably by Lees, Donaldson, Honda and Simidu, and others. Lees heated one end of the bar electrically and by surrounding the whole bar with a Dewar flask he could measure thermal conductivity down to liquid air temperatures. Honda and Simidu employed the two plate method shown in Fig. 3. P_1, P_2 are two exactly similar plates made of the experimental material. Between these is symmetrically placed the electrical heater H in which the heat Q is generated. For perfect symmetry two cold plates K, K maintained at the same temperature are placed at

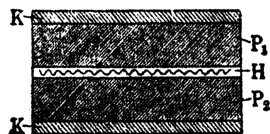


Fig. 3—The two-plate system.

the other ends of these plates. Thus the amount of heat flowing through each plate is $Q/2$.

II. Conductivity from Temperature Measurement—Indirect method

6. Rectilinear Flow of Heat. Mathematical Investigation.—Consider a metal rod heated at one end, the isothermal surfaces being parallel planes perpendicular to the length of the rod, and let the axis of x be normal to these planes. At a distance x from the hot end (Fig. 4) let θ be the temperature and $\frac{d\theta}{dx}$ the temperature gradient, and consider a layer of thickness dx at this point. The amount of heat Q_1 which enters the layer per second is $-KA\frac{d\theta}{dx}$ (from equation 2), Q_2 the heat which leaves the layer at the face $x+dx$ is

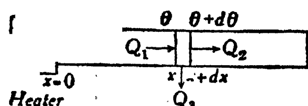


Fig. 4.—Flow of heat in a rod.

$$-KA\frac{d}{dx}\left(\theta+\frac{d\theta}{dx}dx\right), \quad . \quad . \quad . \quad . \quad (3)$$

since $\theta+\frac{d\theta}{dx}dx$ is the temperature of that face. Hence the gain of heat by the layer is equal to

$$-KA\frac{d\theta}{dx}-\left[-KA\frac{d}{dx}\left(\theta+\frac{d\theta}{dx}dx\right)\right]=KA\frac{d^2\theta}{dx^2}dx. \quad . \quad (4)$$

Now before the steady state is reached this amount of heat raises the temperature of the layer of thickness dx. Let ρ be the density and c the specific heat of the material per unit mass, and let the rate of rise of temperature be denoted by $\frac{d\theta}{dt}$. The mass of the layer is $\rho A dx$. Hence, neglecting the heat lost by radiation from the surface, we get

$$KA\frac{d^2\theta}{dx^2}dx=\rho A dx.\, c\frac{d\theta}{dt} \qquad (5)$$

$$\therefore \frac{d\theta}{dt}=\frac{K}{\rho c}\frac{d^2\theta}{dx^2}=h\frac{d^2\theta}{dx^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $h=K/\rho c$. Thus h is equal to the thermal conductivity divided by the thermal capacity per unit volume. This constant h has been called thermal *diffusivity* by Kelvin and *thermometric conductivity* by Maxwell but the former term is more commonly used. It will be seen that the thermal diffusivity h represents the change of temperature produced in unit volume of the substance by the quantity of heat which would flow in unit time through unit area under unit temperature gradient. Thus for calculations of the rate of rise of temperature the constant h is of greater importance than K as equa-

tion (6) shows (as the rate depends not only on K but also on ρc), but in the steady state the rate of flow of heat depends only on K and not on ρc (see equation 8).

If, in addition, the sides of the bar are allowed to lose heat by radiation, this must be taken into account. If E is the emissive power of the surface, p its perimeter and θ the excess of the temperature of the surface over that of the surroundings, this radiation loss Q_3, assuming Newton's Law of Cooling to hold true, is equal to $Ep\theta\, dx$. Hence we should rewrite (5) as

$$KA\frac{d^2\theta}{dx^2}\,dx = \rho\, Adx.c\,\frac{d\theta}{dt} + Ep\theta\, dx.$$

Or

$$\frac{d\theta}{dt} = h\,\frac{d^2\theta}{dx^2} - \mu\theta, \quad \ldots \quad (7)$$

where

$$\mu = \frac{Ep}{\rho\, Ac}.$$

This is the standard Fourier equation for one dimensional flow of heat and any problem in thermal conduction along a rod consists simply in the solution of this differential equation.

Steady State—A state is said to be steady when the temperature at every point of the rod is stationary, *i.e.*, $\frac{d\theta}{dt}=0$. We have then

$$\frac{d^2\theta}{dx^2} = \frac{\mu}{h}\,\theta = m^2\theta, \quad \ldots \quad (8)$$

where

$$m^2 = \frac{\mu}{h} = \frac{Ep}{AK}$$

If the radiation losses from the sides can be neglected, this equation further reduces to

$$\frac{d^2\theta}{dx^2} = 0.$$

The solution of this differential equation yields

$$\theta = Ax + B,$$

where the constants A and B can be determined from the boundary conditions. Let these conditions be (1) $\theta = \theta_0$ at $x=0$, θ_0 being the temperature of the source; (2) $\theta=\theta_1$ at $x=l$. Then we have

$$\theta = \theta_0 - \frac{\theta_0 - \theta_1}{l}\,x,$$

where θ is the temperature at any point x.

If radiation losses are not negligible, the solution will be different. Let us assume that in this case $\theta = e^{nx}$ is the solution. Hence, by substitution,

$$n^2 = m^2, \text{ or } n = \pm m.$$

Therefore, the complete solution is

$$\theta = Ae^{mx} + Be^{-mx} \quad . \quad . \quad . \quad . \quad (9)$$

where A, B are constants.

7. Ingen-Hausz's Experiment.— A method of comparing the conductivity of different substances based on this solution was employed by Ingen-Hausz as early as 1789 and is generally shown as a demonstration experiment. Bars of different substances are coated with wax and have their one end immersed in a hot bath of oil (Fig. 5). The wax melts to different lengths along different bars. Before the steady state is reached the temperature at any point depends on h, i.e., on both the thermal capacity and the thermal conductivity as indicated by equation (7). This is why initially the temperature wave is observed to travel faster along bismuth than along copper, for the low thermal capacity of the former more than compensates for the larger conductivity of the latter. When the steady state is attained, however, the wax is found to melt on the copper over a greater length.

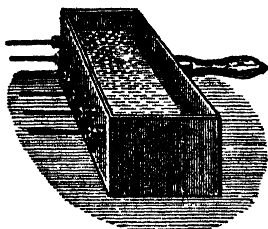


Fig. 5.—Apparatus of Ingen-Hausz.

Let, l_1, l_2 . . . . . denote the lengths along which the wax has melted on the different bars, θ_0 the temperature of the bath measured above that of the surrounding, and θ_1, the temperature of melting wax similarly measured. If the bars are long enough the temperature at their other ends is the same as that of the surroundings, *i.e.*, $\theta=0$. The complete solution of this problem is represented by equation (9). The boundary conditions for all the bars are (*i*) $\theta=0$ at $x=\infty$, (*ii*) $\theta=\theta_0$ at $x=0$, (*iii*) $\theta=\theta_1$ at $x=l$.

By substitution in equation (9) condition (*i*) gives $A=0$. Condition (*ii*) then gives $B=\theta_0$. The solution then becomes

$$\theta = \theta_0 e^{-mx}.$$

Condition (*iii*) then gives

$$\theta_1 = \theta_0 e^{-ml}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or

$$ml = \log_e \frac{\theta_0}{\theta_1}.$$

Since $\log_e(\theta_0/\theta_1)$ is the same for all the bars we have

$$m_1 l_1 = m_2 l_2 = m_3 l_3 = \ldots = \text{constant},$$

which from the definition of m implies that

$$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \ldots . = \text{constant}, \quad . \quad . \quad (11)$$

provided the different bars have the same cross-section, perimeter and coefficient of emission. Thus

$$\frac{K_1}{K_2} = \frac{l_1^2}{l_2^2}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Therefore the conductivities are in the simple ratio of the squares of the lengths along which the wax has melted, and if the conductivity of one of the bars be known the conductivity of the others can be calculated. This is an indirect method. In order to secure the same coefficient of emission the bars are electroplated and polished.]

8. Experiments of Despretz, Wiedemann and Franz.—Despretz, as early as 1822, compared the conductivity of two substances by means of three temperatures at equal distances. The bars were heated at one end and were provided with a number of equidistant holes throughout their entire length. These holes contained mercury in which the bulbs of mercury thermometers were immersed for recording the temperature. The theory of the method can be worked out with the help of equation (9).

Wiedemann and Franz following the same principle devised a more accurate apparatus. The bars under test were about half a metre long and 6 mm. in diameter and were electroplated. One end of the bar was heated by steam and the remainder surrounded by a constant-temperature jacket. The temperatures at equidistant points were measured by a sliding thermo-couple which could be manipulated from outside.

III. Conductivity by a Combination of the Steady and Variable Heat Flow

9. Forbes' Method.—One of the earliest methods of determining the absolute conductivity of a substance is that due to Forbes.*

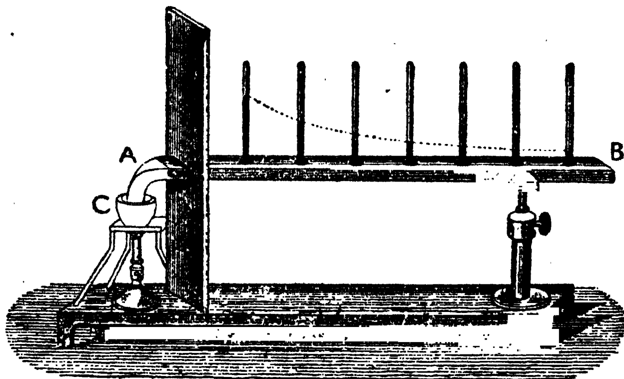


Fig. 6.—Forbes' apparatus. Statical experiment.
(The dotted curve shows fall of temperature along the bar and tangent to the curve gives the temperature gradient).

Though simple in principle, it is exceedingly tedious in practice. Forbes used a bar of wrought iron 8 ft. long and $1\frac{1}{4}$ inch square section. One end of the bar (Fig. 6) was heated by being fixed into an iron crucible

* James David Forbes (1809-1868) was Professor of Natural Philosophy in the University of Edinburgh from 1833 to 1860.

containing molten lead or silver. A number of thermometers, with their bulbs immersed in holes drilled into the bar, were employed to indicate its temperature throughout its entire length. After about six hours the temperatures at all points become steady and are read on the thermometers. The temperature distribution is indicated by the dotted line in Fig. 6, and follows the law $\theta = \theta_0 e^{-mx}$. This is called the *statical experiment* since it deals with the steady state of heat flow.

To obtain the heat flowing across a particular cross-section, Forbes determined the amount of heat lost by radiation by the portion of the bar lying between that cross-section and the cold end. These two quantities are obviously equal in the steady state since no heat flows out from the cold end, this being at the room temperature. Forbes achieved it by performing the *dynamical experiment*, so called because the temperature in this case is changing. For this purpose a bar only 20 inches long but in all respects exactly similar to the previous bar was used. First a high uniform temperature is communicated to this bar which is then allowed to cool in exactly the same surroundings as the statical bar, and a cooling curve plotted for it (Fig. 7).

Let us now calculate the amount of heat lost by the statical bar from the point $x = x_1$, to the end of the bar ($x = l$). The amount of heat lost per second by radiation from the surface of the bar from x to $x + dx$ in the steady state, is

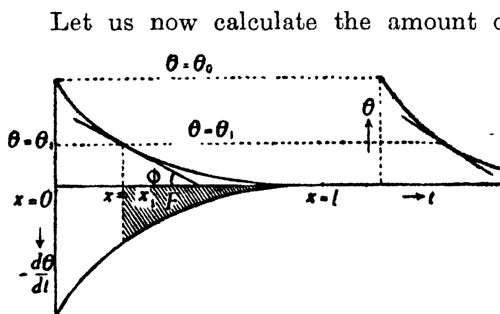


Fig. 7.—Temperature curves in Forbes' bar.

$$-A dx . \rho c \frac{d\theta}{dt}$$

where ρ is the density of the material, c its specific heat and $-\frac{d\theta}{dt}$ the rate of cooling of that element. Hence the total heat lost by the portion of the bar from $x = x_1$ to $x = l$ in a second is

$$-A\rho c \int_{x=x_1}^{x=l} \frac{d\theta}{dt} \, dx$$

This will also be equal to the heat crossing the surface at $x = x_1$, *viz.*,

$$-KA \left(\frac{d\theta}{dx} \right)_{x=x_1}$$

since the bar is long enough so that its other end is at the room temperature and hence there is no loss of heat from that end. Equating

these two quantities we have

$$\frac{K}{\rho c}\left(\frac{d\theta}{dx}\right)_{x=x_1} = \int_{x=x_1}^{x=l} \frac{d\theta}{dt}\,dx. \qquad . \quad . \quad . \quad (13)$$

For calculating $\frac{d\theta}{dt}$ the dynamical experiment is performed on an exactly similar specimen with the same exposed surface. The observations are plotted in Fig. 7 which is self-explanatory. The θ, x and θ, t curves are drawn from actual observations while the values of $-\frac{d\theta}{dt}$ corresponding to various values of θ are computed from the θ, t curve and plotted as indicated. Equation (13) yields

$$\frac{K}{\rho c}\tan\phi = F,$$

where $\tan\phi$ and F are indicated in the figure. The area F of the shaded portion can be measured by means of a planimeter and hence K calculated.

There are several sources of error in Forbes' method and hence the method fails to give accurate results. The specific heat does not remain constant at different temperatures as assumed by Forbes. Further the distribution of temperature inside the bar in the statical and dynamical experiments are different. Forbes' method has been improved by Callendar, Nicholson, Griffiths and others.

IV. CONDUCTIVITY BY PERIODIC FLOW METHOD

10. Angstrom's Method.— The conductivity of a metallic bar can also be found by periodically heating and cooling a portion of the bar and observing the temperature at different times at two points along the bar. This method was first employed by Angstrom.*

In his early experiments a small portion of the bar was enclosed in a chamber through which steam and water at any temperature could be alternately passed. In later experiments the end instead of the middle was heated. The bar was heated for 12 minutes and cooled also for the same time, the periodic time being 24 minutes. Temperatures were observed every minute at two points along the bar by means of two thermocouples. The mathematical analysis of this case is somewhat complicated and will not be given here. We have to solve equation (6) such that the solution is a periodic function of time.

11. Conductivity of the Earth's Crust.— The periodic flow method is very suitable for finding the conductivity of the earth's crust. The earth's surface is heated by day and cooled by night. This alternate heating and cooling effect travels into the interior of the earth in the

* Anders Jonas Angstrom (1814-1874) was Professor of Physics at Upsala. He made important researches in heat, magnetism and optics.

form of a heat wave (*diurnal wave*) and gives rise to the *diurnal* variations in temperature at points inside the earth's crust. Again, the earth receives a larger amount of heat in summer than in winter and this causes a second heat wave having the period one year (*annual wave*) which is also propagated into the interior of the earth. Assuming the waves to be simple harmonic as a first approximation (the annual wave, in particular, departs considerably from this ideal state), let us find how they travel into the earth. The problem is that of a bar periodically heated and cooled at one end and provided with a guard-ring ($\mu=0$).

A simple harmonic solution of (6) is

$$\theta = \theta_0 e^{-\alpha x} \sin(\omega t + \beta x + \gamma), \qquad . \quad . \quad . \quad (14)$$

which gives the temperature fluctuations at any point x. This is the equation of a damped progressive wave and is graphically represented in Fig. 8. The wave moves forward with the velocity $-\omega/\beta$ while its amplitude goes on diminishing exponentially (given by $\theta_0 e^{-\alpha x}$) which is shown by the dotted curve. These fluctuations will be superposed on the mean temperature at any point which will also diminish as we go farther from the hot end.

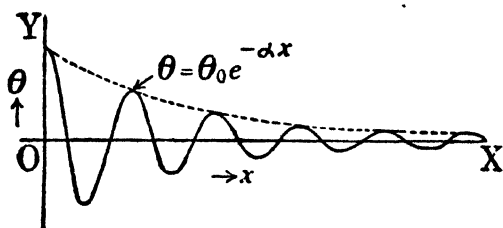


Fig. 8.—Temperature wave at a particular instant.

It can be easily seen that the *wave-length of the temperature wave* is $\lambda = -2\pi/\beta$. Again, by substitution from (14) in (6) we get

$$\alpha = -\beta, \qquad h = \frac{\omega}{2\beta^2} = \frac{\lambda^2}{4\pi T} \quad . \quad . \quad . \quad . \quad (15)$$

Hence $$\alpha = \sqrt{\pi/hT}.$$

Now if a number of thermometers are embedded in the earth at different depths, the progress of the temperature wave inside the earth can be investigated, and knowing the wave-length, the diffusivity h can be calculated from (15). In the same way we can find the conductivity of any bar if we heat one end in a simple harmonic manner as was done by King.

12. Applications.—The above mathematical treatment can be utilised for solving the geological problem, *viz.*, the penetration of the daily and annual changes of temperature within the earth's crust. It will be easily seen from (14) that the range of amplitude R at any point is

$$R = 2\theta_0 e^{-x\sqrt{\pi/hT}}$$

and velocity of propagation

$$v = -\frac{\omega}{\beta} = 2\sqrt{\frac{\pi h}{T}} \quad . \quad . \quad . \quad (17)$$

and wave-length $\lambda = 2\sqrt{\pi h T}$. . . . (18)

The "lag." *i.e.*, the time which any temperature applied at the surface takes to travel to a point x is

$$t = \frac{x}{v} = \frac{x}{2}\sqrt{\frac{T}{\pi h}}.$$

We shall now apply these results to the propagation of heat inside the earth's crust. Here for the daily wave

$$T = 24 \text{ hours} = 86400 \text{ sec.}$$

Taking $h = 0{\cdot}0049$, the value for ordinary moist soil, we have

$$\lambda = 73 \text{ cm.} \; ; \; v = 8{\cdot}4 \times 10^{-4} \text{ cm./sec.} \; ; \; \alpha = 1/11{\cdot}6.$$

Suppose the maximum temperature is 45°C. at 2 P.M. and the minimum is 25°C. just after sunrise, the amplitude of temperature variation is, therefore, 20°C. This variation will diminish as $e^{-x/11\cdot 6}$ at a depth x. For $x = 10$ cm., $e^{-x/11\cdot 6} = {\cdot}42$, for $x=30$, $e^{-x/11\cdot 6} = {\cdot}076$ and for $x = 100$, $e^{-x/11\cdot 6} = {\cdot}00018$. Thus at a depth of 1 metre the temperature variations will be scarcely noticeable.

The slow velocity of penetration of the daily heat wave must have been familiar to all observant minds in a tropical country. Here the roof of the house is exposed to the scorching heat of the sun, and at 2 P.M. the temperature may be as great as 60°C. But this temperature travels inward at the extremely slow rate of $9{\cdot}1 \times 10^{-4}$ cm./sec. or 6·4 cm. per hour in a mass of concrete ($h = 0{\cdot}0058$). Hence to penetrate a wall depth of 30 to 40 cm. a period of 5 or 6 hours is necessary. The inside of the room, provided the windows are shut, therefore, reaches its maximum temperature at about 7 or 8 P.M. when the walls become intolerably hot and begin to radiate. Most people must have experienced that it is found impossible to sleep indoors at this time. The minimum at the top of the room is reached at about sunrise. So the rooms are found to be cool from 11 A.M. to about 2 P.M. when the outside is hot.

Annual Wave.—Besides the diurnal fluctuations the surface of the earth is also subject to an annual period of 365¼ days owing to the different amount of surface heating in winter and summer. This amount is variable in different countries, but in desert countries it may amount to as much as 60°C in the sun in summer and 0°C. in winter.

In the case of the annual wave

$$\lambda = 73\sqrt{365/1} = 73 \times 19{\cdot}1 \text{ cm.} = 14 \text{ metres}$$

$$v = 8{\cdot}4 \times 10^{-4}\sqrt{1/365} \text{ cm./sec.} = 3{\cdot}9 \text{ cm. per day.}$$

$$\alpha = \frac{1}{11{\cdot}6}\sqrt{\frac{1}{365}} = \frac{1}{220}.$$

Thus the annual wave will penetrate a depth of about 1·2 metres in a month. At a depth of $x = \lambda/2 = 7$m. the times of the year are interchanged. The amplitude of temperature variation will be reduced by the fraction $e^{-100/220} = \cdot 64$ at 1 metre depth and by $e^{-1000/220} = \cdot 011$ at 10 metres depth. Thus the annual wave is able to penetrate to a depth which is $\sqrt{365/1}$ = about 19 times greater than the daily wave. Most of these conclusions have been verified experimentally.

13. Conduction through Composite Walls.—If a wall is made up of a number of slabs of thicknesses x_1, x_2 . . . and conductivities K_1, K_2 . . . joined together, the amount of heat flowing per second through an area A of the wall in the steady state is

$$Q = \frac{\theta_1 - \theta_2}{\frac{x_1}{K_1 A}} = \frac{\theta_2 - \theta_3}{\frac{x_2}{K_2 A}} = \ldots\ldots$$

where θ_2, θ_3...are the temperatures of the intermediate surfaces and θ_1, θ_n are the temperatures of the end faces. This is because in the steady state the same amount of heat must flow through each

$$\theta_1 - \theta_2 = Q \frac{x_1}{K_1 A}; \quad \theta_2 - \theta_3 = Q \frac{x_2}{K_2 A}; \ldots .$$

and by addition

$$\theta_1 - \theta_n = Q \left(\frac{x_1}{K_1 A} + \frac{x_2}{K_2 A} + \ldots \right)$$

Therefore the heat flowing per second is

$$Q = \frac{\theta_1 - \theta_n}{\frac{x_1}{K_1 A} + \frac{x_2}{K_2 A} + \ldots\ldots} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

14. Relation between the Thermal and Electrical Conductivities of Metals. Wiedemann-Franz Law.— A table of thermal conductivities is given on p. 200. The table shows unmistakably that all good conductors of electricity are also good conductors of heat, and even before any theory was proposed, Wiedemann and Franz gave the empirical law that *the ratio of thermal and electrical conductivities at a particular temperature is the same for all metals.* Lorenz extended the law and showed that this ratio is proportional to the absolute temperature, *viz.*, $K/\sigma T$ = constant, where K is the thermal conductivity and σ the electrical conductivity.

Drude explained this remarkable result by assuming that the conduction of heat and electricity in metals takes place by means of free electrons. He even found theoretically the value of $K/\sigma T$.

These conclusions have been experimentally verified by Jaeger and Diesselhorst and by Lees. They obtained the value of $K/\sigma T$ experimentally for various metals which are given in Table 1. It

will be seen that the value of $K/\sigma T$ remains practically constant for all metals.

Table 1.—Values of $\frac{K}{\sigma T} \times 10^8$.

Metal	From Lees' experiment				Jaeger and Diesselhorst	
	−170°C.	−100°C.	0°C.	17°C.	10°C.	100°C.
Aluminium ...	1·50	1·81	2·09	2·13	2·19	2·27
Copper ...	1·85	2·17	2·30	2·32	2·29	2·32
Silver ...	2·04	2·29	2·33	2·33	2·36	2·37
Zinc ...	2·20	2·39	2·45	2·43	2·31	2·33
Cadmium ...	2·39	2·43	2·40	2·39	2·43	2·44
Tin ...	2·48	2·51	2·49	2·47	2·53	2·49
Lead ...	2·55	2·54	2·53	2·51	2·46	2·51
Iron ...	3·10	2·98	2·97	2·99	2·76	2·85
Brass ...	2·78	2·54	2·45	2·45	...	...
Manganin ...	5·94	4·16	3·41	3·34	3·14	2·97

A closer examination of the table shows that the value falls off at low temperatures. Now at these temperatures both the thermal and electrical conductivities are found to increase. Hence it follows that the thermal and the electrical conductivities do not increase in the same ratio when the temperature falls, the electrical conductivity increasing much more rapidly. In fact, the latter appears to become extremely large at the absolute zero, if the metal is free from impurities.

15. Heat Conduction in Three Dimensions.—Till now we have considered the flow of heat in one direction only, generally along bars of great length but small width and thickness. We shall now consider the conduction of heat in three dimensions inside an isotropic body. It can be shown by an amplification of the ideas given in sec. 6 that for flow in three dimensions, the equation of conduction is given by

$$K\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)=\rho c\,\frac{d\theta}{dt},$$

or

$$h\nabla^2\theta=\frac{d\theta}{dt} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where h is the diffusivity. This is the Fourier equation of heat conduction in general and we can solve it when the initial conditions are given. Equation (20) is of great importance in studying problems on heat conduction.

V. CONDUCTIVITY OF POORLY CONDUCTING SOLIDS

16. In finding the conductivity of poor conductors the substance cannot be employed in the form of long bars or rods as was the case with metals, for the heat loss from the sides would be considerable compared with the heat actually conducted away through the substance itself. For this reason the substance is generally used in the form of thin plate, sphere or cylinder. To this class belong all non-metallic bodies. Cork, asbestos, clay, wood, bricks, etc. are among the many substances of common occurrence. The conductivity of these varies from 0·01 to 0·00008. We shall now give some of the important methods of finding the conductivity of these substances.

In the methods commonly employed for finding conductivity of poorly conducting solids, energy is supplied electrically to a separate heating body, and the flow of heat through the experimental substance investigated.

17. Spherical Shell Method.— The simplest case of heat conduction in three dimensions is that of a sphere. If the source of heat is placed at the centre of the sphere the isothermal surfaces will be spherical surfaces described about the centre. The method has been employed by Nusselt and others. Nusselt's apparatus is shown in Fig. 9. The external hollow sphere A is 30 cm. in diameter and made of copper. Inside it and concentric with it, is another hollow sphere C of aluminium, 15 cm. in diameter. The spheres can be split into two and reunited. The space between the spheres is filled with the material B under test such as asbestos, powdered cork, charcoal etc. An electrically heated body D is placed at the centre of the sphere inside C and electrical energy is supplied at a constant rate. Temperatures are determined by means of thermo-couples placed in B at different distances from the centre and along one or more radii. Knowing the electrical energy spent and the radii of the shells, the conductivity can be calculated.

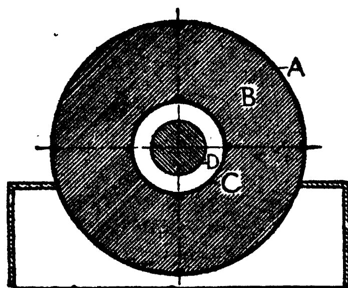


Fig. 9.—Nusselt's apparatus.

We shall solve the problem from elementary principles. On account of the symmetry about the centre the isothermal surfaces are spherical. The flux of heat across a spherical surface of radius r outwards in unit time is $-K.\ 4\pi r^2 \frac{d\theta}{dr}$. This must equal the amount of electrical energy Q supplied per second to the heating body. Hence*

* We can also proceed as in sec. 6.

$$Q = -4\pi K r^2 \frac{d\theta}{dr}.$$

Or $$d\theta = -\frac{Q}{4\pi K}\cdot\frac{dr}{r^2}. \qquad (21)$$

Since Q is independent of r we have on integrating (21)

$$\theta = \frac{Q}{4\pi K}\cdot\frac{1}{r} + A, \qquad (22)$$

where A is a constant of integration.

If the two surfaces of the shell of radii r_1, r_2 acquire temperatures θ_1, θ_2 in the steady state, we have

$$\theta_1 = \frac{Q}{4\pi K}\cdot\frac{1}{r_1} + A, \quad \theta_2 = \frac{Q}{4\pi K}\cdot\frac{1}{r_2} + A,$$

whence $$Q = \frac{4\pi K(\theta_1 - \theta_2) r_1 r_2}{r_2 - r_1}.$$

Knowing Q, θ_1, θ_2 and r_1, r_2 as in the above experiment the conductivity K can be calculated. Again, solving the simultaneous equations for Q and A, and substituting these values of Q and A in (22), the temperature distribution in the material can also be found, and is given by the expression

$$\theta = \frac{1}{r_2 - r_1}\left[(r_2\theta_2 - r_1\theta_1) + \frac{(\theta_1 - \theta_2) r_1 r_2}{r} \right]. \qquad (24)$$

18. Cylindrical Shell Method.— Let us consider the radial flow of heat in a cylinder which has an electrically heated wire along its axis. By suitably transforming equation (20) we can get the equation for this case. We shall, however, as before, deduce it from elementary considerations. Since the cylinder is symmetrical about its axis, the isothermal surfaces are cylindrical. The amount of heat Q flowing per second across an isothermal surface is

$$Q = -2\pi r l . K \frac{d\theta}{dr}, \qquad (25)$$

where l is the length of the cylinder. Now Q must remain constant, being equal to the electrical energy supplied per second. On integrating between the inner and outer radii of the cylindrical shell with corresponding temperatures θ_1, θ_2, we have,

$$2\pi l K(\theta_1 - \theta_2) = Q \log_e(r_2/r_1),$$

or $$K = \frac{Q}{2\pi l}\cdot\frac{\log_e (r_2/r_1)}{\theta_1 - \theta_2}. \qquad (26)$$

The temperature θ at a distance r can be shown to be given by

$$\theta = \frac{1}{\log (r_2/r_1)}\left[(\theta_1 \log r_2 - \theta_2 \log r_1) - (\theta_1 - \theta_2) \log r \right] \qquad (27)$$

Niven has devised a method of determining conductivities based on this method. The cylinder of the material is formed by filling the

space between two hollow concentric cylinders with that material. Heat is supplied by a wire carrying an electric current along the axis of the cylinder, and when the steady state is reached, temperatures at two points within the material are observed, as well as their distance from the axis. Knowing the electrical energy spent, equation (26) gives the conductivity.

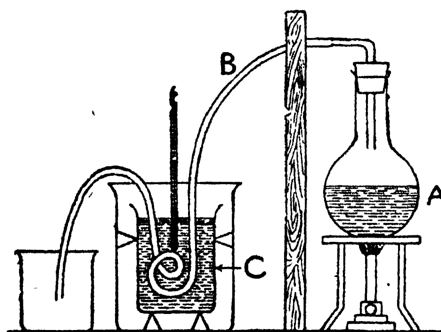


Fig. 10.—Apparatus for finding conductivity of rubber.

A simple laboratory experiment based on this method may be devised for finding the conductivity of rubber and glass in the form of a tube. For rubber the arrangement shown in Fig. 10 is most convenient. Steam from the boiler A traverses through a rubber tube B, a length l of which is immersed in a weighed amount of water contained in the calorimeter C. The radial flow of heat Q from the tube to the water in C is given by

$$Q = \frac{2\pi Kl(\theta_1 - \theta_2)}{\log_e (r_2/r_1)} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where θ_1 represents the temperature of steam, and θ_2 the mean of the initial and final temperatures of the calorimeter. This heat can be calculated from the rise in temperature of the calorimeter and its thermal capacity, and hence equating these two quantities we get K, provided r_1, r_2 are known*.

For glass the arrangement shown in Fig. 11 is convenient. The glass tube C has a spiral wire along its axis and is surrounded by a steam jacket, while a steady current of water flows though the tube. The method of calculation is similar to the preceding one.

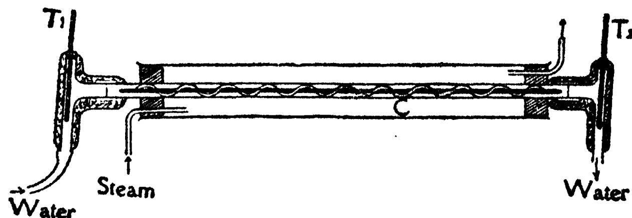


Fig. 11.—Apparatus for finding conductivity of glass.

19. Lees' Disc Method.— Another convenient method for finding the conductivity of a very bad conductor has been given by Lees in which the substance is used in the form of a thin disc. The

* For experimental details see Worsnop and Flint, *Practical Physics*.

apparatus (Fig. 12), due to Lees and Charlton, consists of a cylindrical steam chest A, the bottom of which is a thick brass block B in which a hole is bored for inserting a thermometer T_1. The substance S (shown shaded), in the form of a circular disc, is sandwiched between the block B and a second cylindrical brass block C, the latter carrying a second thermometer T_2. The block C is suspended from a retort stand by threads so that its top face is horizontal.

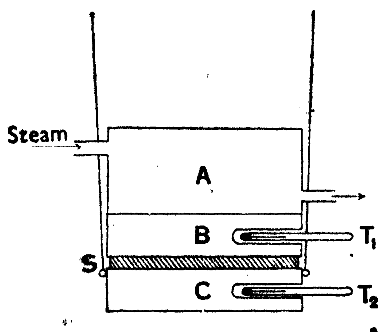


Fig. 12.—Lees' disc method for bad conductor.

The radius and the thickness d of the specimen are first measured. The apparatus is then set up as shown in Fig. 12 and steam is passed through A for a pretty long time until the readings in the thermometers T_1 and T_2 are steady. These temperatures can be taken to denote the temperatures θ_1 and θ_2 of the upper and lower ends of the specimen as brass is an extremely good conductor of heat. Since the temperature of C is steady, the rate at which heat is received by it from conduction through the specimen must be equal to the rate at which heat is lost by it by radiation from the sides and the bottom surface of C. The former is given by

$$Q = KA\frac{\theta_1 - \theta_2}{d}, \qquad \ldots \qquad (29)$$

where K is the required conductivity and A the area of the disc. The latter is determined in the following way:—

The block C is alone heated separately by a bunsen burner until its temperature rises to about 10°C above θ_2. It is then alone suspended with the specimen placed on the top and allowed to cool. Its temperature is noted at regular intervals of time until it cools to about 10°C below θ_2 and a cooling curve drawn. From the tangent to the curve at θ_2, the rate of cooling $-\frac{d\theta}{dt}$ at θ_2 is determined. The rate of loss of heat by cooling is

$$Q = -ms\left(\frac{d\theta}{dt}\right)_{\theta=\theta_2} \qquad (30)$$

where m and s denote respectively the mass and the specific heat of the block C. Combining (29) and (30), K can be found.

In the above we have assumed that no heat is lost from the curved surface of the specimen, and consequently the specimen must be very thin.

The disc method can also be used with electric heating when a modified arrangement is necessary. A thin plate of the experimental

substance is placed between two copper plates. A coil of insulated wire is placed above the upper copper plate and held down by another copper plate as explained later in §22. Electrical energy is supplied to the coil and steady state obtained. The amount of heat passing through the experimental disc can be obtained from the electrical energy supplied and the loss of energy due to surface emission. Knowing the temperature of the copper plates the conductivity can be calculated. Alternatively, the two-plate system can be employed by placing above the heater coil another sandwiched experimental plate, exactly similar to the system below the heater coil. In this arrangement it is not necessary to know the radiation loss as all the electrical energy is transmitted through the two specimens.

CONDUCTIVITY OF LIQUIDS

20. The determination of the conductivity of a liquid is complicated by the presence of convection currents. If we heat a column of liquid at the bottom, the liquid at the top receives heat both by conduction and convection. The laws governing convection currents are complicated, hence it is preferable to eliminate them. This is accomplished either by taking a column of liquid and heating it at the top or by taking a thin film of liquid.

21. Column Method.— The column method was employed by Despretz long ago. The liquid at the top was kept heated and temperatures along the axis of the column were observed by mercury thermometers. He found that Fourier's equation already derived for a bar holds true in this case also, and hence the conductivities of two liquids can be compared with the help of equation (11). Weber surrounded the column with a guard-ring and used as the source of heat an electrically heated oil bath. The bottom of the column was cooled by a copper plate standing in ice. The heat conducted away was found from the amount of ice melted. Knowing the temperature distribution along the column the absolute conductivity can be calculated in the same manner as for mercury in Berget's experiment.

22. Film Method.— This was employed by Lees, Milner and Chattock and by Jakob. We shall describe the apparatus used by Lees which is simply a modification of his disc method for finding the conductivity of poor conductors. The liquid L under test is enclosed in an ebonite ring E (Fig. 13) and placed between copper blocks C_1, C_2. To determine the quantity of heat flowing through the liquid a glass disc G is inserted, above which another copper plate C_3 is cemented with a layer of shellac. Above C_3 and insulated from

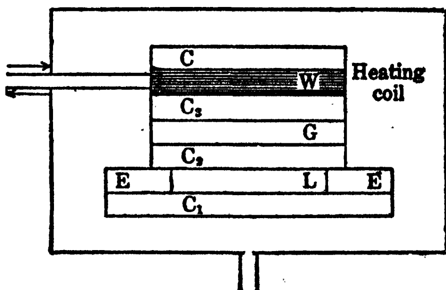


Fig. 13—Lees' apparatus for finding the conductivity of liquids.

it by mica is placed a flat spiral coil of heating wire W which is held down by another copper plate C. The whole pile is varnished and enclosed in an air-bath. Temperatures are recorded by thermocouples soldered to the faces of the copper plate. The calculations can be easily made.

Let S_1, S_2, S_3, S_G denote the emitting surfaces of C_1, C_2, C_3 and G respectively, h their emissivity and T_1, T_2, T_3 the temperatures of the copper discs. The heat passing through the middle section of G is by definition equal to $AK_G(T_3 - T_2)/d_G$. Of this the amount $\frac{S_G h}{2} \cdot \frac{T_3 + T_2}{2}$ is lost by the lower half of G by radiation from the sides and similarly $S_2 h T_2$ is lost by C_2. Hence the heat transmitted through the liquid and the ebonite is equal to

$$AK_G \frac{T_3 - T_2}{d_G} - S_G h \frac{(T_3 + T_2)}{4} - S_2 h T_2$$

and thus must evidently be given by

$$K_L A_L \frac{T_2 - T_1}{d_L} + B(T_2 - T_1),$$

where B is some constant giving the transmission of energy through the ebonite E for unit difference of temperature. Equating these two expressions we get K_L in terms of K_G provided B is known. B can be determined by working with air whose conductivity is known.

23. Hot-wire Method.—Goldschmidt employed the "hot-wire" method of Andrews and Schleiermacher, the theory of which is discussed in sec. 18. The liquid was contained in a silver capillary tube 2 mm. in diameter heated by a wire running along its axis.

CONDUCTIVITY OF GASES

24. The determination of the conductivity of gases is difficult for the phenomenon is always accompanied by radiation, and sometimes by convection currents also. Kundt and Warburg showed that the rate of cooling of a thermometer immersed in air remained constant for pressures lying between 150 mm. and 1 mm. Hence the effect of convection currents is negligible in this region and heat is lost only by conduction and radiation. To determine the radiation loss, the air was exhausted as completely as possible, and then the rate of cooling was found to be independent of the size of the enclosure, showing that the effect of conduction was negligible and heat was lost only by radiation. Subtracting this radiation loss, we get the heat lost by conduction alone. For finding the conductivity of a gas at pressures higher than 150 mm. the gas may be exhausted to this pressure (between 150 mm. and 1 mm.) and its conductivity determined. Now since the conductivity of a gas is independent of the pressure (see Chapter III, Sec. 24) this will give the required conductivity. Another

procedure consists in taking a thin film of gas and heating it at the top when convection will be absent.

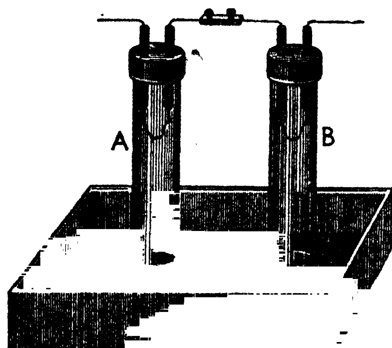


Fig. 14—Apparatus to show the better conductivity of hydrogen.

A very simple experiment described by Andrews and Grove shows qualitatively that hydrogen is a far better conductor of heat than any other gas. A fine platinum wire was supported inside a glass tube (Fig. 14) which could be filled with any gas. The wire could be heated by an electric current and made to glow. Two such tubes were arranged side by side, one filled with air and the other with hydrogen. The same electric current was allowed to flow through both the wires. The wire in the air-tube can be seen glowing while the wire in the hydrogen tube does not glow at all. The glass tube containing hydrogen also becomes hot. Heat is very quickly conducted away by hydrogen and hence the wire is not raised to the temperature of incandescence. Replacing hydrogen with air restores the incandescence.

The important methods of finding the absolute conductivity of a gas are—

(1) Hot-wire Method, (2) Film Method.

25. Hot-wire Method.— This method, first given by Andrews, was employed by Schleiermacher for determining the absolute conductivity of a gas. An electrically heated vertical wire is surrounded by a coaxial cylinder filled with the experimental gas. The temperature of the wire is known from its resistance, and the amount of heat flowing across the curved surface of the cylinder is found from the rate of energy supplied to the wire. The conductivity can be calculated from equation (26) where r_1, r_2 now denote the radii of the wire and the tube respectively. In this arrangement convection is very much minimised since there is no temperature gradient in the vertical direction. Radiation losses and whatever convection losses remain, are eliminated as pointed out in sec. 24. Correction must, however, be applied for loss of heat by thermal conduction along the leads supplying the electrical current. The method has recently yielded very accurate and reliable values for a large number of gases.

26. Film Method.— The film method, originally used by Todd, has been employed by Hercus and Laby. The principle underlying it is the same as in Lees' experiments (sec. 22). The thin film of gas under test was enclosed between two copper plates B and C (Fig. 15),

the latter of which was cooled by a current of water. The upper plate B was made up of two sheets of copper clamped together with a heating coil between them. To prevent loss of heat by radiation from the upper surface of B, there was another plate A above it at the same temperature and a guard-ring D surrounding it. On account of the latter the flow of heat from B to C was linear. The plates A, B, D contained separate heating coils and thermocouples and were kept at the same temperature. The thermocouples were formed by attaching constantan wires to the copper plates, each plate having a copper lead also attached to it. The plates were accurately ground and silver-plated. The whole apparatus was made air-tight by a ring of rubber clamped to A and C by steel bands. The temperature of A was gener-

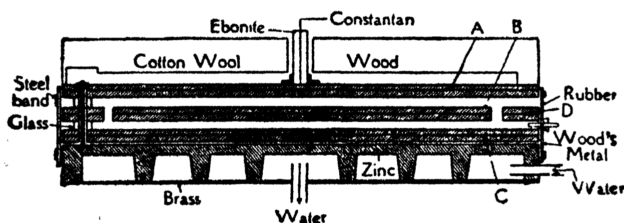


Fig. 15—Apparatus of Hercus and Laby.

ally kept a little above that of B in order to eliminate any possibility of convection. This, however, necessitated a small correction. The radiation correction was determined by a separate experiment on a silvered Dewar flask and was only about 5 per cent. Convection effects are entirely absent since the gas is heated at the top. The energy spent in B was known electrically and subtracting from it the heat lost by radiation, the heat transmitted to C by conduction through the air film was found. Knowing the temperature of C the conductivity of the gas can be calculated from equation (1).

27. Results.— The thermal conductivity of a number of substances is given in Table 2, p. 200. The value of K is given in calorie cm.$^{-1}$ sec.$^{-1}$ °C^{-1}.

It will be seen from the table that silver is the best conductor of heat ($K=1$) and copper comes next. The conductivity is less for liquids and least for gases. The conductivity of gases is extremely low (of the order of 10^{-5}).

We have already considered on p. 85, Chap. III, the relation between thermal conductivity and viscosity of gases, as well as the variation of the thermal conductivity of gases with pressure.

Table 2.—Thermal conductivities of different substances.*

Substance	Conductivity
Metals (0°C.)	
Aluminium ...	0·48
Cadmium ...	0·23
Copper ...	0·93
Iron (pure) ...	0·16
Lead ...	0·085
Mercury ...	0·025
Nickel ...	0·14
Silver ...	1·0
Platinum ...	0·17
Tin ...	0·155
Zinc ...	0·265
Alloys (0°C)	
Brass ...	0·23
Constantan ...	0·05
Manganin ...	0·05
German silver ...	0·06
Poorly Conducting Solids (18°C.)	
Crown glass ...	$2{\cdot}5\times10^{-3}$
Flint glass ...	2

Substance	Conductivity
Asbestos paper ...	$0{\cdot}6\times10^{-3}$
Cardboard ...	0·5
Cork ($\rho = \cdot16$) ...	0·11
Paper ...	0·3
Ebonite ...	0·42
Mica ...	1·8
Paraffin wax ...	0·6
Pine wood ...	0·4
Rubber ...	0·45
Liquids.	
Water (24°) ...	$14{\cdot}3\times10^{-4}$
Alcohol (25°) ...	4·3
Glycerine (25°) ...	6·8
Gases (0°C.)	
Hydrogen ...	$31{\cdot}8\times10^{-5}$
Helium ...	33·9
Argon ...	3·89
Air ...	5·40
Oxygen ...	5·63
Carbon dioxide ...	3·07

28. Freezing of a pond.—An interesting example of conduction across a slab of varying thickness is provided by the phenomenon of freezing of water in ponds and lakes during winter. When ice begins to form on a pond, the bulk of the water in the pond is at about 4°C while the top layers are at 0°C, and the cold air above abstracts the latent heat from a narrow surface layer at 0°C. The subsequent growth of the ice layer requires that the necessary abstraction of latent heat takes place by conduction through the layer of ice already there. Assume that the thickness of the ice layer already formed is z, and the temperature of the water below this layer is 0°C. Then for a further freezing of the layer of area A and thickness dz in the time dt, the quantity of heat

$$Q = A\rho dz . L$$

* Taken partly from Landolt and Bornstein, *Physikalish-Chemischen Tabellen* and partly from Kaye and Laby, *Tables of Physical and Chemical Constants.*

must travel upwards by conduction through ice of thickness z, where $\rho =$ density of ice and L = the latent heat of fusion. Hence

$$Q = KA \frac{0-(-\theta)}{z} dt,$$

where K = thermal conductivity of ice, and $-\theta$ is the temperature of the air above the pond. Equating we get

$$zdz = \frac{K\theta}{\rho L} dt,$$

which on integration yields

$$\tfrac{1}{2}z^2 = \frac{K\theta}{\rho L} t,$$

the constant of integration being zero as $z=0$ at $t=0$. Thus the time to obtain a given thickness is proportional to the square of the thickness.

Exercise.—The thickness of ice on a lake is 5 cm and the temperature of the air is $-20°$C. Find how long it will take for the thickness of the ice to be doubled. (For ice thermal conductivity is 0·005 cal. cm^{-1} sec.$^{-1}$ °C^{-1}, density = 0·92 gm./c.c., latent heat = 80 cal./gm.)

[We have

$$\tfrac{1}{2}\Big[z^2 \Big]_5^{10} = \frac{K\theta}{\rho L}\Big[t \Big]_0^t$$

or

$$t = \frac{10^2-5^2}{2} \frac{\rho L}{K\theta}$$

$$= \frac{10^2-5^2}{2} \frac{0{\cdot}92\times 80}{0{\cdot}005\times 20}$$

$$= 27{,}600 \text{ sec} = 7^h 40^m.]$$

CONVECTION OF HEAT

29. Natural and Forced Convection.—We have already stated in § 20 and § 24 that there will be transfer of heat by convection in fluids unless proper precautions are taken. Convection is the transference of heat by heated matter which moves carrying its heat with it. Thus it can take place only in fluids. *Free or natural convection* always takes place vertically and is caused by gravity as a consequence of the change in density resulting from the rise in temperature and consequent expansion. In *forced convection* a steady stream of fluid is forced past the hot body by external means. Still-air cooling is natural convection; ventilated cooling in a draught is forced convection.

The theoretical treatment of convection is rather complicated though the problem of forced convection is a little simpler. Nevertheless convection is of great practical importance. The land and

sea breezes, the trade winds, the fall of temperature with height in the atmosphere (discussed fully in Chap. XII) are all examples of convection on a huge scale in nature. The ventilation of rooms and the central heating of buildings in winter are some examples of forced convection in every-day life.

30. Natural Convection.— When a heated body is cooled in air, all the three methods of heat transference are acting simultaneously. But the air is a very poor conductor of heat, and radiation is important only for large differences of temperature; thus the chief means of heat loss is convection. The mechanism of this heat loss is easy to understand but the derivation of a theoretical formula is extremely difficult. The problem is therefore best studied experimentally or by a recourse to the method of dimensions.

In the film theory of cooling by convection the mechanism of heat loss is somewhat as follows:—It is believed that the whole surface of the cooling body is covered by a thin layer of stagnant fluid adhering to the surface. In natural convection this film is permanently present while in forced convection this is being continuously wiped off and renewed. Thus in natural convection the heat has to flow across this film of air and the amount lost will depend upon the thermal conductivity of the air and the temperature difference between the body and the air. The heat transmitted will raise the temperature of the air causing convection which will be opposed by viscous forces. Thus the heat loss will depend upon the specific heat, expansion coefficient and viscosity of the air.

An elaborate series of experiments on natural convection was performed by Dulong and Petit. They observed the rate of cooling of a thermometer in a large copper globe surrounded by a bath at a fixed temperature. The experiments were first done with the globe evacuated when the heat loss was due to radiation alone and the rate of fall of temperature was found to be

$$-\frac{d\theta}{dt} = k(a^{\theta} - a^{\theta_0}), \quad . \quad . \quad . \quad . \quad (31)$$

where k is a constant depending upon the nature of the surface and θ, θ_0 the temperature of the thermometer and the enclosure respectively. Next the globe was filled with different gases at different pressures, and rate of cooling observed. Subtracting from this the radiation loss, the loss due to convection alone was computed and found to be

$$-\frac{d\theta}{dt} = mp^{c}\,(\theta-\theta_0)^{1\cdot233}. \quad . \quad . \quad . \quad (32)$$

where p is the pressure of the gas and m, c are constants depending upon the gas. Thus the rate of loss of heat due to natural convection can be written in the form

$$-\frac{d\theta}{dt} = k'(\theta-\theta_0)^{5/4}. \quad . \quad . \quad . \quad . \quad (33)$$

where k is a constant depending upon the gas and its pressure, and 5/4 has been written instead of 1·233. This is called the five-fourths power law for natural convection which can be also deduced theoretically.

For forced convection experiments show that the rate of loss of heat is proportional to the temperature excess $(\theta-\theta_0)$. It will be thus seen that Newton's law of cooling holds for forced convection even for large temperature differences but is not true for natural convection. As shown in Chap. XI it holds for radiation provided the temperature difference is small.

Books Recommended.

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. I.

2. Ingersoll and Zobel, *Mathematical Theory of Heat Conduction* (Ginn, 1913).

3. Carslaw and Jaeger, *Conduction of Heat in Solids* (1947), Clarendon Press, Oxford.

CHAPTER IX

Heat Engines

1. Introduction to Thermodynamics.— Thermodynamics is literally the science that discusses the relation of heat to mechanical energy. But in a broad sense, it comprises the relation of heat to other forms of energy also, such as electrical and chemical energy, light energy, etc. The principles of Thermodynamics are very general in their scope, and have been applied widely to problems in Physics, Chemistry and other sciences. The theory of heat engines forms an integral part of the subject, and as the early developments were largely in connection with the problem of conversion of heat energy to mechanical work, we shall begin the study by devoting a chapter to the Theory of Heat Engines.

HEAT ENGINES*

2. The progress of civilisation has been intimately bound up with man's capacity for the development and control of power. History tells us that whenever man has been able to make a great discovery leading to a substantial increase in his power, a fresh epoch in civilisation began.

The present age has sometimes been styled as the 'Steam Age' indicating the profound influence exerted by the invention of the 'Steam Engine' on the course of human progress. In this chapter, we shall make a brief survey of this "great event."

At the present time we know that Heat is a kind of motion. Whenever motion disappears it reappears as heat, and experiments show that 1 calorie of heat is equivalent to $4 \cdot 18 \times 10^7$ ergs of work. The question naturally arises: "Can we not reverse the process? Can we not by some contrivance, convert heat which is in so much excess about us, to useful work ?"This is in fact the function of heat engines which we are going to discuss. They are contrivances to convert heat to work.

But the early investigators were profoundly ignorant of the "Nature of Heat" hence the problem did not present itself to them in this form. They, however, observed that generally when bodies get heated, they develop power. We may take three examples familiar to every body:—

1. When water is boiled in a closed kettle, the lid is blown off by steam generated inside. This shows that high pressure steam can be made to do work.

* In preparing this chapter, we have drawn very freely from the admirable little book by Prof. E. N. da C. Andrade on "Engines" and we wish at this place to acknowledge our grateful thanks to the author.

2. When gunpowder or any explosive is exploded a sudden impulse is created which may be utilised for throwing stones, cannon balls and for breaking rock.

3. High velocity wind can be made to do work, *e.g.*, from early times sails have been used for the propulsion of ships, for driving mills (wind-mills). We know that such winds are due to intensive heating of parts of the earth's surface by the sun.

The three illustrations chosen above have served as the starting point for three different classes of engines which convert heat to work, *viz*: (1) the steam engine widely used for locomotion and in industry, (2) the internal combustion engines used in motor cars, aeroplanes, and for numerous other purposes, (3) the windmills and steam and gas turbines.*

Many of the principles utilised in these engines are quite common to all classes, and we shall begin by describing the evolution of the steam engine. Though the mechanical details are outside the scope of this book, an elementary discussion is included for the sake of completeness and continuity of treatment.

3. Early History of the Steam Engine.— The earliest record of human attempt to make a heat engine is found in the writings of Hero of Alexandria, a member of the famous Alexandrian school of philosophers (300 B.C.—400 A.D.) which included such famous men of science of antiquity as Ptolemy (astronomer), Euclid (geometer) and Eratosthenes (geographer). Hero describes a scientific toy in which air was heated in a closed box and allowed to expand through a pipe into a vessel below containing water. The water was thus forced up through another pipe into a vertical column producing an artificial fountain. There was, however, no suggestion to employ it on a large scale. In 1606, about two millenia after Hero, Marquess Della Porta, founder of the Neapolitan Academy and one of the pioneers of scientific research in Europe, employed steam in place of air in Hero's experiment in order to produce a fountain. He also suggested that in order to fill up the vessel with water, it may be connected by a pipe to a water reservoir below. If the vessel filled up with steam be now cooled with water from the outside, steam inside will condense, a vacuum will be produced, and water will be forced up from the reservoir, replenishing the vessel again. This principle was utilised by Thomas Savery in 1698 to construct a water-pumping machine which is described below. He was the first man to produce a commercially successful steam engine which was extensively used for pumping water out of mines, and supplying water from wells.

The principle utilised in this engine is illustrated in Fig. 1 (p. 206). V is a steam boiler, A, B and C are valves. The operation takes place in two stages :—

* Recently during the second world war a new type of engine based on the rocket principle was developed in Germany and Italy. In these a high velocity jet of air escapes at the rear of the machine which on account of the reaction thus produced moves forward with tremendous velocity.

(a) B is kept closed and A, C are open. Steam passes from V to P and forces the water to D.

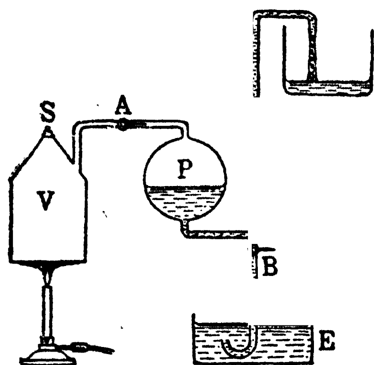


Fig. 1.—Principle of Savery's engine.

(b) A and C are closed, and B opened. Cold water is sprinkled on P. This condenses steam in P, a vacuum is created and water is sucked up from the pit E to P. After this the operation (a) may be again performed and a fresh cycle begun.

Savery's engine could not suck water through more than 34 feet, but it could force up the water to any height. In fact, he sometimes forced up water to a height of 300 feet. This means that he used high pressure steam up to 10 atmospheres. This was a risky procedure though Papin had shown about 1680, how the risk in using high pressure steam could be minimised by the introduction of the safety valve.

Papin, a French settler in England, had discovered a method of softening bones by boiling them in a closed vessel under pressure. This, as we know, raises the boiling point of water to about 150°C and makes the water a very powerful solvent. Papin invented the safety valve which he attached to the boiler to prevent his vessel from being blown up by high pressure steam. This is shown in Fig. 2.

The *safety valve* consisted of a rod LM pivoted at L and carrying a weight N at the other end. It pressed down the valve P which exactly fitted the top of the tube HH leading from the inside of the boiler. Whenever the steam pressure exceeded a certain limit, it forced up the valve P and the excess steam would rush out. By adjusting the weight of N or its distance from L, the maximum steam pressure could be regulated at will.

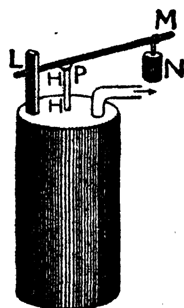


Fig. 2.—Papin's Safety Valve.

4. Newcomen's Atmospheric Engine.—The next forward step was the invention of Newcomen's Atmospheric Engine which was designed to pump out water from mines and wells, and was in practical use for more than fifty years. This engine is interesting from the historical point of view since it directly led to the great inventions of James Watt, and it employed for the first time, the cylinder and the piston, which has been a feature of steam engines ever since. Fig. 3 illustrates the Newcomen Engine.

A is the cylinder, T is the piston suspended by a chain from the lever pivoted to masonry works. The other arm of the lever carries the piston rod W of the water pump which goes into the well. There is a counter-weight M to balance the weight of the piston T. The problem is to move the piston T up and down.

This was achieved as follows:—Starting with the piston T at the bottom of A, steam is introduced from the boiler B which forces the piston up till it reaches the top. The steam is shut off by the tap D, and cold water sprayed through F which condenses the steam in the cylinder. Vacuum is produced inside the cylinder and consequently the atmospheric pressure forces down the piston, D is again opened and a fresh cycle begins. The water in the cylinder A drains out through a side pipe.

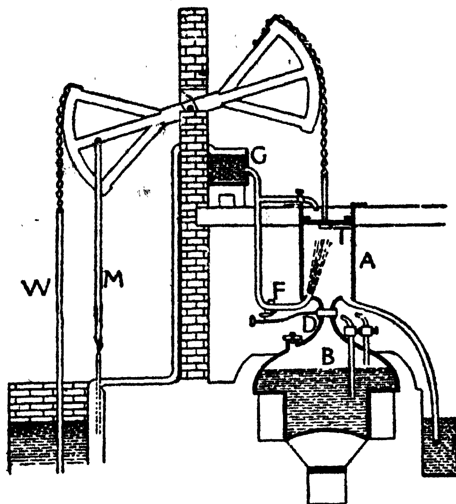


Fig. 3.—Newcomen's Atmospheric Engine.

For closing and opening the valves automatically, a parallel motion guide was provided which carried mechanism for automatically operating the valves. The story goes that the invention was due to a lazy boy who was employed to close and open the valve by hand, but who tied a parallel rod to the swinging arm of the lever, and connected it by means of cords to the valves, and leaving this rod to do his work enjoyed himself all the while in playing. Whatever may be the origin, the parallel guide has been a permanent feature of steam engines ever since.

In the Newcomen Engine, the useful work is done by the atmospheric pressure while steam is only employed to produce vacuum, hence the name *atmospheric engine*. It is easily seen that it is very wasteful of fuel.

5. James Watt.— James Watt is commonly credited with the discovery of the steam engine. The circumstances which directed his attention to steam engine are pretty well known. He was an ingenious scientific instrument maker at Glasgow, and in 1763 he was asked by the professor of Physics at the Glasgow University to repair a Newcomen Engine belonging to them which had never worked well. While engaged in the repair of this machine, the idea occurred to him that the Newcomen Engine was awfully wasteful of fuel, and being of an inventive temperament, he began to ponder and experiment on the production of a better type of machine. He was thus

led to a series of investigations and contrivances which gave the steam engine its present form and rendered it a mighty factor in the onward march of industry and civilisation. We are describing some of his inventions below.

6. Use of a Separate Condenser.— Watt observed that a large part of the expansive power of steam is lost on account of the fact that the cylinder is alternately heated and cooled. The expansive power of steam depends upon its temperature. Now when the steam enters the cylinder, which has been previously cooled to create a vacuum, some heat is taken up by the cylinder in becoming heated and is not converted into useful work. The temperature of steam falls and its expansive power is diminished. Another disadvantage in using the cylinder as condenser is that cold water entering the cylinder becomes heated and exerts appreciable vapour pressure, thus preventing the formation of a good vacuum. The problem was to condense the steam without cooling the cylinder. Watt achieved this by the use of a separate condenser.

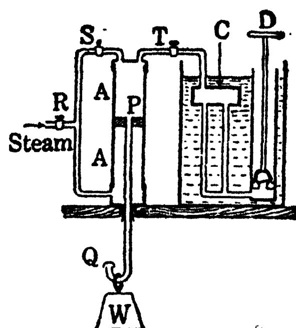


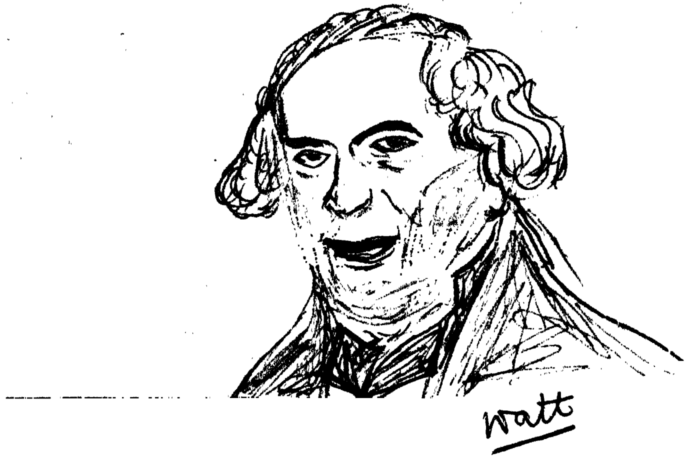
Fig. 4.—Watt's Experimental Condenser.

The principle of the separate condenser is illustrated in Fig. 4. AA is the cylinder in which the piston P moves to and fro. The piston is provided with a hollow tube PQ carrying a valve Q at the end such that Q allows steam to go out but is closed by the atmospheric pressure when there is vacuum inside. Starting with the piston P at the bottom of the cylinder, R, S are opened and the part of the cylinder above P is filled with steam, forcing out the air and residual steam through Q. Then S is closed and T opened. The steam is drawn into the condenser C which had been previously evacuated by the pump D, and is there condensed by the cold water surrounding the condenser. Consequently a vacuum is produced above P and steam from below pushes the piston P upwards, doing work on the weight W. Then T is closed, S opened and P is drawn down to the bottom by W and the cycle begins afresh. The pump D serves to remove the air and water produced from steam in C.

To keep the cylinder hot, Watt further surrounded the cylinders by a steam box and wood. Now-a-days the cylinders are jacketted with asbestos or some badly conducting substance, and then covered with thin metal sheets.

7. The Double-acting Engine.— In the Newcomen engine we have seen that the atmosphere pushes down the piston. Shortly afterwards Watt employed steam instead of the atmosphere to push the piston down. The raising of the piston in the subsequent stroke was brought about by a counter-weight attached to the other arm of

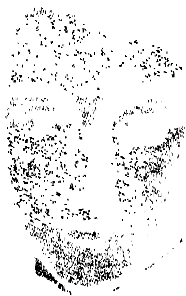
To face p. 208





WATT (p. 207)

James Watt, born in Scotland in 1736, died in 1819. His important work is the masterly perfection of the steam engine which increased the powers of man ten times and ushered the 'Industrial Revolution.'



CARNOT (p. 213)

Nicolas Leonard Sadi Carnot, born on June 1, 1796 in Paris, died of cholera on August 24, 1832. He introduced the conception of cycle of operations for heat engines and proved that the efficiency of a reversible engine is maximum.

the beam. For these operations to be possible the upper end of the cylinder must be closed. Watt achieved this by means of a steam-tight *stuffing box* which is full of oily tow. This is kept tightly pressed against the piston so that the piston can move through the cover without loss of steam. This was the so-called *single-acting engine* of Watt. Watt, however, soon realised that in this engine no work was done by steam during that stroke in which the piston was raised up by the action of the counter-weight. He saw that the power could be approximately doubled if during this useless stroke, steam is admitted to the lower side and the upper side is connected to the condenser. This is achieved in the *double-acting engine*, invented by Watt, with the aid of a number of valves. A modern double-acting cylinder provided with valves is shown in Fig. 5. The cylinder has ports or holes A, B, near its each end and between these lies another port E leading to the exhaust or condenser. To the cylinder is fastened the steam chest C containing the D-*slide valve* S. Steam from the boiler enters the steam chest at the top. In the position (*a*) steam enters the cylinder through the port B and pushes the piston to the left, thereby driving the steam in front through A to the exhaust E. As the piston moves to the left the slide valve moves to the right and

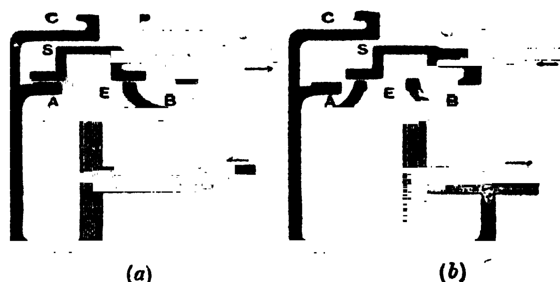


Fig. 5.—Double-acting cylinder with slide valve.

closes both the ports A and B for a time, and later when the piston reaches the extreme left position, B is closed and A opened. Steam then enters through A forcing the piston backward and driving the steam in front to the exhaust. This is shown at (*b*). The double-acting engine is now universally employed in all kinds of steam engines.

The timely action of the slide valve is adjusted by means of an eccentric wheel attached to the moving shaft (see Fig. 7). In powerful engines as in locomotives the slide valve is often replaced by a piston valve which is very similar.

8. Utilisation of the Expansive Power of Steam.—Watt's another great invention was the so-called expansive working of steam. He saw that if steam is allowed to enter the cylinder all the time the piston is moving outwards, the steam pressure in the cylinder will be the same as in the boiler and though we get a powerful stroke, the expansive power of steam is not utilised. If, however, the steam

is cut off when the piston has moved some distance, the piston would complete its journey by the expansive power of steam, whose pressure will in consequence be reduced to almost that of the condenser. Thus more work is obtained from the same amount of steam by allowing the steam to expand adiabatically and hence the running of the machine becomes considerably economical. It is thus of great advantage to use high pressure steam.

It was mentioned in the last section that the slide valve closes both the ports A and B when the piston has moved some distance. From this instant to the end of the stroke the steam is allowed to expand adiabatically.

9. The Governor and the Throttle Valve.— Another simple but very useful invention of Watt was that of the governor. This is a piece of self-acting machinery which controls the supply of steam from the boiler into the cylinder, and ensures smooth running of the engine at a constant speed.

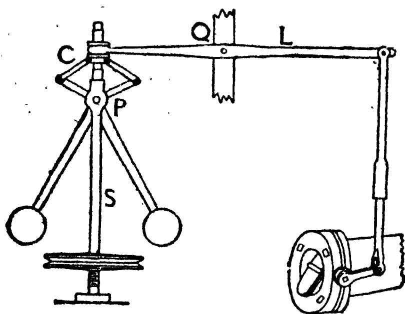


Fig. 6.—Watt's governor with throttle valve.

Watt's governor is shown in Fig. 6. S is a vertical spindle which is made to revolve by means of gearing from the engine shafts. Its speed, therefore, rises or falls with the engine speed. It carries a pair of heavy balls which are fastened to S by rods pivoted at P. The balls rise on account of centrifugal force as the spindle rotates, and as they do so they pull down a collar C which slides smoothly in the spindle S. The collar C fits into one end of a lever L, pivoted at Q. The other end is connected to a tap in the steam pipe called the throttle valve. As C is pulled down, the throttle valve tends to close the tap, the steam supply falls off, and the engine speed falls. If the engine speed is too much diminished, the balls fall down, C is pushed up, and the throttle valve opens admitting more steam, and the speed goes up. Thus the governor automatically regulates the speed at which the engine runs. Improved forms of governors are now employed in engines.

10. The Crank and the Flywheel.—Watt was the first to convert the to-and-fro motion of the piston into circular motion by means of the connecting rod and the crank. Thus the steam engine can be made to turn wheels in mills, work lathes and drive all kinds of machinery in which a rotary motion is needed.

The connecting-rod R and the crank C are shown in Fig. 7 at (*a*). The crank is a short arm between the connecting-rod and the shaft S. The connecting-rod is attached to the piston rod and consequently takes up the to-and-fro motion of the latter. As the connecting-rod moves forward it pushes the crank and thereby rotates the shaft S. In the return stroke the circular motion is

completed. There are, however, two points in each revolution when the connecting-rod and the crank are in the same line and the piston exerts no turning moment. These are called the 'dead centres.' At two points when the crank is at right angles to the connecting-rod the torque is maximum. To prevent the large variation in the magnitude of the torque producing variations in the speed of the shaft during a single revolution a big flywheel F, shown at (*c*), is attached to the shaft. The flywheel on account of its large moment of inertia carries the crank shaft across the dead centres; in fact, it absorbs the excess of energy supplied during a part of the half-revolution and yields back the same in the remaining part of the half-revolution when less energy is supplied. Thus the flywheel acts as a reservoir of energy which checks variations during a single stroke, while the governor prevents variations from stroke to stroke.

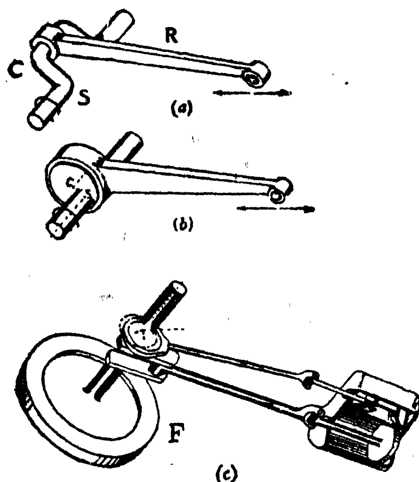


Fig. 7.—Crank, Eccentric and Flywheel.

Another mechanism to convert the to-and-fro motion into circular motion or vice versa is the eccentric, shown at (*b*), Fig. 7. It consists of a disc mounted off its centre on the shaft S and surrounded by a smoothly fitting collar to which the rod is attached. The behaviour is as if there was a crank of length SC. Such an eccentric is mounted on the shaft carrying the flywheel (shown at *c*) and works the slide valve. The effects can be properly timed by suitably mounting the eccentric on the shaft.

The essential parts of a simple engine are shown in Fig. 8. They will be easily followed from the figure.

11. Modern Steam Engines.— Since the time of Watt many important innovations have been introduced into the steam engine though the main features remain the same. The innovations were needed in order to suit the circumstances of ever-widening application of steam engines to various purposes. Watt always used steam engines with low steam pressure, and of a static type. He was evidently afraid of explosions. But engines using low pressure steam are comparatively inefficient, as we shall see presently, and in modern times high pressure engines have almost replaced the old Watt engines necessitating the construction of special type of boilers.

Condensers in modern engines consist of a number of tubes containing cold water kept in circulation by means of a pump, and

are further provided with a pump to remove the air and water produced by steam on condensation.

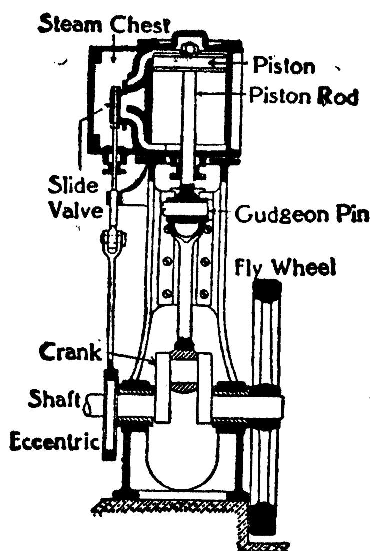


Fig. 8.—Main parts of a Steam Engine.

Again in powerful engines the high pressure steam is not allowed to expand completely in a single cylinder. The steam is partly expanded in one cylinder and passed on to one or more cylinders where the expansion is completed. Such engines are known as compound engines and may consist of three or four cylinders.

Richard Trevithick was the first to construct a 'locomotive,' i.e., a steam engine which could draw carriages on rails. He could not, however, push his inventions to financial success. It was left to George and Robert Stephenson, father and son, to construct the first successful locomotive—the "Rocket", and run the first railway train in 1829, between Liverpool and Manchester. Robert Fulton was the first to apply the steam engine to ships in 1812.

12. Efficiency of Engines and Indicator Diagrams.—The earlier inventors of steam engine had no clear idea of the Nature of Heat, and being engineers rather than physicists, they did not make serious attempts at understanding the physical processes involved in the running of a steam engine. They measured efficiency by finding out the quantity of coal which had to be burnt per unit of time in order to develop a certain power. This was rather a commercial way of measuring efficiency.

An absolute measurement of efficiency is obtained from the first law of thermodynamics. A heat engine is merely an apparatus for the conversion of heat to work. The heat supplied is obtained by finding out the calorific value of the fuel consumed by burning a sample of the fuel in a bomb calorimeter (p. 63). If Q be the calorific value of the fuel consumed per unit of time and W the power developed, we can define the economic efficiency η as the ratio between Q and W, viz., $\eta = W/JQ$. Accordingly η is the fraction of the heat converted to work.

For an ideal engine, η should be unity. But actual experience shows that η is rather a small fraction. In Watt's days, it was only 5%; now-a-days even in the best type of steam-engines, it hardly exceeds 17%.

The question arises whether this lack of perfectness is to be ascribed to the bad designing of heat engines, or whether there is

something in the very nature of things which prevents us from converting the whole amount of heat to work.

This question was pondered over by Sadi Carnot about a hundred years ago. He showed that even with an ideal engine, it is never possible to convert more than a certain percentage of heat to work.

It is very convenient to represent the behaviour of an engine by an indicator diagram and hence in discussing the theory and performance of heat engines this is always done. Suppose a certain amount of gas is contained in a vessel at a certain temperature and pressure and occupies a certain volume. Evidently the state of the substance is uniquely represented by assigning its pressure and volume. Thus we can represent the state of the gas by a point A (Fig. 9) on a graph such that the abscissa of the point represents the volume of the gas and the ordinate represents the pressure.

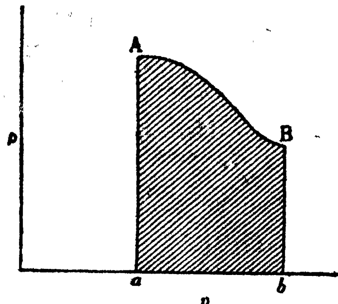


Fig. 9.—The indicator diagram.

Let the pressure and the volume of the gas be changed to that corresponding to the point B and suppose the pressure and the volume throughout this change are represented by points on the line AB. Then this operation is represented by the line AB on this diagram. Such *p-v* diagrams are known as *indicator diagrams*.

As proved on p. 46 the work done by the gas in expanding against a pressure p is $p\delta v$. In this case since p changes from point to point the total work done by the gas in expanding from v_a to v_b is equal to $\int_{v_a}^{v_b} pdv$ and is evidently equal to the area A*ab*B. The work is taken to be positive if the diagram is traced in the clockwise direction. It is thus clear that the indicator diagram directly indicates the work done by the engine during each cycle of operations, the work being equal to the area enclosed by the indicator diagram. Indicator diagrams are therefore of great use in engineering practice.

The indicator diagram gives the work performed by the piston per stroke. Multiplying it by the number of strokes per second *i.e.* by twice the number of revolutions of the shaft we get the power indicated by the indicator which is generally expressed in horse-power —*indicated horse-power*. The power actually delivered by the engine is measured by a brake dynamometer and is called the *brake horse-power*, the ratio of this to the indicated horse-power is called the *mechanical efficiency* of the engine.

13. The Carnot Engine.— As we have seen, the function of the steam engine is to convert the chemical energy stored in coal to energy of motion by utilising the expansive power of steam.

The machinery necessary for this purpose is, however, so complicated that one is apt to lose sight of the essential physical principles in the details of mechanical construction. Let us, therefore, discuss the physical principles involved in the running of a heat engine. Three things are apparently necessary, *viz.*, a source of heat, a working substance, and machines. In the steam engine, the source of heat is the furnace where heat is supplied by the burning of coal. But we may get heat by a variety of other means, *e.g.*, by burning oil, wood, naphtha, or even directly from the sun (solar engines), or from the inside of volcanoes (as is sometimes done in Italy). We can, therefore, replace the furnace by the general term "reservoir of heat." For steam, we can use the general term "working substance," for any substance which expands on heating can be used for driving heat engines. As a matter of fact, we have got hot air engines in which air is heated by a gas burner or a kerosene lamp, and pushes the piston up and down as steam would do.

In addition to the three requisites mentioned above, we require a fourth one, viz., the possibility of having a temperature difference. This at first is not so apparent, but can easily be made clear. In a hot air engine, the heated air can push the piston outward since the air outside is at a lower temperature. If there were no difference of temperature, no difference of pressure could be created, hence the machine would not work. We, therefore, require not only a source of heat, but also a sink, *i.e.*, a heat reservoir at a lower temperature. In steam engines the surrounding air acts as the sink of heat or condenser.

Carnot observed that the function of the machine is to extract a certain quantity of heat Q from the heat reservoir F, convert a part of it to work and transfer the rest to the heat sink G. He also showed how these operations should be carried out so that the efficiency may be maximum.

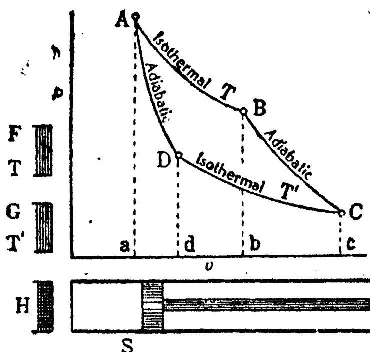


Fig. 10.—The ideal Carnot engine with indicator diagram.

Since whenever there is a difference of temperature, there is a possibility of converting heat to work, the converse is also true, *i.e.* if we allow heat to pass from F to G by conduction, we miss our opportunity of getting work. Hence we must extract heat from F in such a way that loss of heat by conduction is reduced to a minimum. Carnot, therefore, thought of the following ideal arrangement.

F is a heat reservoir at temperature T (Fig. 10), G a heat-sink at T', S is the cylinder of the engine containing a perfect gas instead of steam as the working substance and fitted with a non-conducting piston. The walls of the cylinder

are impervious to heat but the bottom is perfectly conducting. The behaviour of the working gas is shown by the indicator diagram showing the pressure and the volume of the gas at any instant. Let the following steps be performed :—

(1) Let the initial temperature of the gas within S be T and let it be placed in contact with F, and the piston moved forward slowly. As the piston moves, the temperature tends to fall, and heat will pass from F to S. The operation is performed very slowly, so that the temperature of the gas is always T. The representative point on the indicator diagram moves from A to B along an isothermal curve. The heat Q extracted in this process is equal to the work done by the piston in free expansion, and is given by

$$w_1 = Q = \int_A^B pdv = RT \log_e \frac{v_B}{v_A} = \text{area AabB.} \quad . \quad . \quad (1)$$

(2) F is then removed and H, which is simply a non-conducting cap, is applied to the cylinder, and the piston allowed to move forward (by inertia). Then the gas will describe the adiabatic BC and will fall in temperature. We stop at C when the temperature has fallen to T'. The work done by the gas is given by

$$w_2 = \int_B pdv = \int_B \frac{\ldots}{v^\gamma} = \frac{\ldots}{1-\gamma}\left[\frac{\ldots}{v_C^{\gamma-1}} - \frac{\ldots}{v_B^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[p_C v_C - p_B v_B\right] = \frac{R(T-T')}{\gamma-1} = \text{area BbcC.} \qquad (2)$$

where $pv^\gamma = K = p_C v_C^\gamma = p_B v_B^\gamma$.

Since the pressure is now very much diminished, the gas has lost its expansive power, hence in order to enable it to recover its capacity for doing work it must be brought back to its original condition. To effect this we compress the gas in two stages: first, isothermally along the path CD, and then adiabatically along DA. The point D is obtained by drawing the isothermal T' through C, and the adiabatic through A.

(3) During the isothermal compression, the cylinder is placed in contact with the sink G at T'. The heat which is developed owing to compression will now pass to the sink. This is equal to the work done on the gas and is equal to

$$w_3 = Q' = \int_D^C pdv = RT' \log_e \frac{v_C}{v_D} = \text{area CcdD.} \quad . \quad . \quad (3)$$

(4) The cylinder S is now placed in contact with H and the gas is compressed adiabatically. The work done on the gas by adiabatic compression is

$$w_4 = \int_A^D pdv = \frac{R}{\gamma-1}(T-T') = \text{area DdaA.} \quad . \quad . \quad (4)$$

It is thus seen that $w_2 = w_4$.

The net work done by the engine

$$W = w_1 + w_2 - w_3 - w_4 = \text{area ABCD}. \quad (5)$$

$$= w_1 - w_3 = Q - Q'. \quad (6)$$

The last result can be written down directly from the first law of thermodynamics.

Since B and C lie on the same adiabatic, we have by equation 24, p. 48,

$$Tv_b^{\gamma-1} = T'v_c^{\gamma-1}$$

or

$$\frac{v_c}{v_b} = \left(\frac{T}{T'}\right)^{1/(\gamma-1)}. \quad (7)$$

Similarly, $\frac{v_d}{v_a} = \left(\frac{T}{T'}\right)^{1/(\gamma-1)} = \rho$, the adiabatic expansion ratio.

Hence

$$\frac{v_b}{v_c} = \frac{v_a}{v_d},$$

or

$$\frac{v_b}{v_a} = \frac{v_c}{v_d} = r, \text{ the isothermal expansion ratio.}$$

We have, therefore,

$$Q = RT \log r, \quad Q' = RT' \log r$$

and

$$W = Q - Q' = R(T - T') \log r. \quad (8)$$

Hence

$$\frac{Q}{T} = \frac{Q'}{T'} = \frac{W}{T - T'}. \quad (9)$$

or

$$W = Q\left(\frac{T - T'}{T}\right). \quad (10)$$

Thus the efficiency of the Carnot engine is

$$\eta = \frac{W}{Q} = \frac{T - T'}{T} = 1 - \frac{T'}{T}. \quad (11)$$

$$= 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad (12)$$

Having analysed the mode of operation of the Carnot cycle, we now proceed to show that (1) it is reversible at each stage, (2) that no engine can be more efficient than the Carnot engine, (3) that the nature of the working substance is immaterial.

14. Reversible and Irreversible Processes.—A *reversible* process is one which can be retraced in the opposite direction so that the substance passes through exactly the same states in all respects as in the direct process. Further, the thermal and mechanical effects at each stage should be exactly reversed, *i.e.*, the amounts of heat received and of work done in each step should be the same as in the direct process, but with opposite sign. That is, where heat is absorbed in the direct process it should be given out in the reverse process and *vice versa*, and where work is done by the working substance in the direct process, an equal amount of work should be

done on the working substance in the reverse process. Processes in which this does not take place are called *irreversible*.

For greater clarity we may add some examples of reversible processes. The transfer of heat from one body to another can be reversible only when the two bodies are at the same temperature. In case of two bodies at different temperatures, the transfer of heat occurring by conduction or radiation cannot be reversed and the process is irreversible.

We shall now consider examples of reversible processes. It is clear from the above definition that the process of bringing an elastic substance into a definite state of stress very slowly is reversible because for a given strain the substance has always a definite stress. A convenient mechanical example of a reversible process is afforded by the performance of a spring balance in the following way. When the spring is very slowly stretched work is done upon it. If, on the other hand, it is allowed to contract slowly by the same amount, the same amount of work is done by the spring, for the work done in increasing the length of the spring by δl is equal to the product of the force F and δl. Both these quantities depend upon the state of the spring at the instant and will have the same value whether the spring is expanding or contracting. Thus the work done upon the spring in stretching will be equal to the work done by the spring while contracting during the reverse process and the process is reversible. *It is essential, however, that the stretching must be produced or reduced gradually by the application of an external force which should differ infinitesimally at every instant from the stress developed in the spring, otherwise a part of the work will be spent in setting up vibrations of the spring and this will produce irreversibility. Such a process is called a quasi-static process and consists essentially of a succession of equilibrium states.*

The case of elastic fluids is analogous to that of the spring. To every volume of the fluid there corresponds a definite stress or pressure, so that the amounts of work done during a balanced expansion or compression are equal. This is an important example of a reversible process. It is important to note that the expansion should be balanced otherwise whirls and eddies may be set up in the fluid which will gradually subside on account of fluid friction with the production of heat and thus a part of the mechanical work would be lost. Such expansion or contraction may be either isothermal or adiabatic and can be brought about easily by applying pressure on the piston enclosing the fluid and adjusting the pressure to differ from the fluid pressure by an infinitesimal amount.

Examples of irreversible processes are (1) sudden unbalanced expansion of a gas, either isothermal or adiabatic, (2) Joule-Thomson expansion, (3) heat produced by friction, (4) heat generated when a current flows through an electrical resistance, (5) exchange of heat between bodies at different temperatures by conduction or radiation, (6) diffusion of liquids or gases etc. Examples (1) and (2) exhibit internal or external mechanical irreversibility, (4) and (5) exhibit thermal irreversibility, and (6) exhibits chemical irreversibility.

A reversible process may be represented by a line on the indicator diagram (p, v) but an irreversible transformation cannot be so represented.

15. Reversibility of the Carnot Cycle.—It is now important to notice that the Carnot cycle is reversible at each stage, *i.e.*, instead of abstracting the heat Q from a source T and transferring a part Q' to a sink T' and converting the balance $Q-Q'$ to work, we can proceed in such a way that the machine abstracts the heat Q' from the sink at T', then we perform the work W on the machine, and Q is transferred to the source at T. This is done by proceeding along the reverse route ADCBA, *i.e.*, first allowing the gas to expand adiabatically from A to D, then allowing it to expand isothermally from D to C in contact with the sink at T', the heat Q' being extracted in the process. Then we compress the gas adiabatically till we reach the point B (temperature T). Next S is placed in contact with the source, the gas is further compressed isothermally till we reach A, and the heat Q is transferred to the body at the higher temperature T. The machine, therefore, acts as a *refrigerator*, *i.e.*, by performing the work W on it, we are depriving a colder body T' of the heat Q'.

An engine in which the working substance performs a reversible cycle is called a *reversible engine*. Engines in which the cycle is irreversible are called *irreversible engines*. For the Carnot cycle to be reversible it is essential that the working substance should not differ sensibly in temperature from that of the hot body and the condenser when it is exchanging heat with them. There should be no transfer of heat by conduction in the usual sense, for it would be irreversible. This requires that the isothermal processes AB, CD should be described indefinitely slowly, and the source and the condenser must have an indefinitely large capacity for heat so as not to change in temperature during the process.

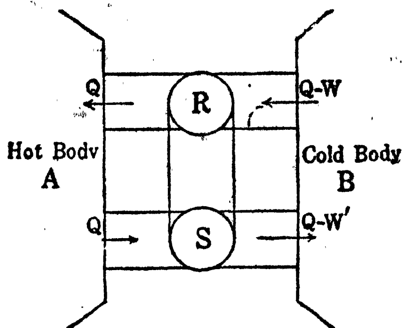
Again the piston should move very slowly without friction. The changes in volume should be brought about by very small changes in the load on the piston in both the isothermal and adiabatic processes, so that the difference between the external pressure and the pressure of the gas should always be infinitesimally small. Thus the Carnot cycle postulates the existence of stationary states of equilibrium while in an actual process the physical state is always changing. Further there should be no loss of heat by conduction from the gas to the piston and cylinder. It will thus be seen that the Carnot cycle with its perfect reversibility is only ideal and cannot be realised in practice.

Nevertheless, it should be noted that for theoretical purposes the deviations from the ideal state may be rightly neglected if they are not an essential feature of the process and if they can be diminished as much as may be desired by suitable devices and then corrected for.

16. Carnot's Theorem.—The idea of reversibility is of the greatest importance in thermodynamics for the reason that, working between the same initial and final temperatures, *no engine can be more*

efficient than a reversible engine. This is known as Carnot's theorem. We now proceed to prove this important theorem.

Suppose we have two engines R and S, of which R is a reversible engine and S an irreversible engine. If possible, let S be more efficient than R. Suppose S absorbs the heat Q from A, converts a part W' to work and returns the rest, *viz.*, $Q-W'$ to the condenser. Let S be coupled to R (Fig. 11) and be used to drive R backwards. We are using R as a refrigerator. It thus abstracts a certain amount of heat from B, has the work W performed on it, and returns the same heat Q to the source A. The amount of heat that R abstracts from B must equal $Q-W$. Now since S is assumed to be more efficient than R, $W'>W$ and hence $Q-W>Q-W'$, *viz.*, R abstracts more heat from B than S restores to it. Thus the net result is that the compound engine RS abstracts heat $(W'-W)$ per cycle from B and converts the whole of it to work, while the source is unaffected. We are thus enabled, by a set of machines, to deprive a body continuously of its heat-content and convert the whole of it to work without producing any change in other bodies. The machine would thus work simultaneously as a motor and a refrigerator and would be the most advantageous in the world. It does not violate the first law for we are creating energy out of heat.



* Fig. 11.—Coupling a reversible and an irreversible engine.

Impossibility of perpetual motion of the second type.—But still the process is quite as good as perpetual motion† of the first kind, for heat is available to us in unlimited amount in the atmosphere, in the soil or the ocean, and if the process were feasible, it would give us all essential advantages of a perpetual motion machine, *viz.*, that of getting work without any expenditure, though not without energy. Human experience forbids us to accept such a conclusion.‡ Hence we conclude that no engine can be more efficient than a reversible engine.

Again, if we assume that a reversible engine using a particular working substance is more efficient than another working with a differ-

* Reproduced from Ewing's *Steam Engine* by the kind permission of Messrs. Macmillan & Co.

† This was a term in use amongst the medieval philosophers who thought that a machine might be invented some day which will create work out of nothing. For some mechanical contrivances which were intended to produce perpetual motion, see Andrade, *Engines*, page 14. The gradual evolution of the Law of Conservation of Energy leading to the first law of thermodynamics showed that the idea is purely chimerical, since energy can never be created out of nothing, but can only be transformed from one form to the other.

‡ This result of human experience is the fundamental basis of the Second Law of Thermodynamics. In fact, Kelvin stated the second law in this form. For fuller discussion, see Chap. X.

ent substance, we arrive by a similar argument at the same absurd result. Hence *the efficiency is the same for all reversible engines and this is the highest limit for the efficiency of any engine that can be constructed or imagined.* This is Carnot's theorem. Thus reversibility is the criterion of perfection in a heat-engine. Hence we see that the efficiency of a reversible engine is maximum and is independent of the nature of the working substance. We chose perfect gas as our working substance, since its equation of state being known, we can easily evaluate η.

NOTE:—It may be mentioned that Carnot was ignorant of the true nature of heat at the time when he published his theorem of efficiency. He followed the old caloric theory in his speculations according to which the quantity of caloric Q contained in a substance was invariable. It was Clapeyron who showed that Carnot's arguments and results remained intact when the Kinetic Theory of Heat was introduced.

17. Rankine's Cycle.—In the steam engine, as we saw in the foregoing pages, the working substance is a mixture of water and water vapour. If, however, we perform the same Carnot cycle with this fluid as with perfect gas the efficiency would also be the same (Carnot's theorem). But the Carnot cycle was performed with the working substance always in the same cylinder. We have already seen that with a view to prevent the wastage of heat consequent on alternate heating and cooling of the cylinder the modern engines are provided with separate boiler, cylinder and condenser. Still, however, if the working substance were to perform the same cycle the efficiency would be the same. But with the organs so separated the adiabatic compression of the working substance in the last stage of the cycle becomes impracticable. Hence the cycle is modified into what is known as Rankine's cycle.

The Rankine cycle is represented in Fig. 12. AB represents the conversion of water into steam in the boiler at temperature T_1 and pressure p_1 and its admission into the cylinder, BC the adiabatic expansion in the cylinder, CD the transfer of steam from the cylinder to the condenser at T_2 and p_2 and its condensation, and DA the transfer by a separate feed-pump to the boiler. This separate feed-pump transfers the condensed water at D at T_2 and p_2 to the boiler and the pressure is consequently raised from p_2 to p_1. At A the water is heated from T_2 to T_1 in the boiler and the cycle begins afresh. The indicator diagram for an engine performing the ideal Rankine cycle is represented by ABCD and this also represents the work done by the engine. The area FADE, usually called the feed-pump term, is extremely small and is generally neglected. The work done by the engine may, therefore, be put equal to the area FBCE. This area can be calculated in much the same

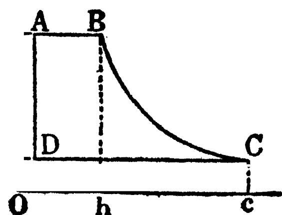


Fig. 12.—The Rankine cycle.

way as on p. 215 if we know the equation of state of steam. This is cumbrous and in engineering practice a simple procedure is adopted.

Let us introduce the total heat function $H = U + pV$. Then

$$dH = dU + pdV + Vdp = Vdp$$

for an adiabatic process, since in this case (Chap. II, § 23) $dU + pdV = 0$.

Integrating between the limits B and C (Fig. 12) we get

$$H_B - H_C = \int_C^B Vdp.$$

The right-hand side represents the area FBCE. Hence the work done in Rankine's cycle per gram-molecule of steam is approximately equal to the heat-drop $H_B - H_C$. This will hold whether the steam is superheated, saturated or wet.

The heat taken in by the working substance is that required to convert water at p_1 and T_2 into steam at p_1 and T_1. This is equal to

$$H_B - [H_D + (p_1 - p_2)V_w] = H_B - H_D \text{ approx.}$$

where H_B, H_D denote the total heat of steam at p_1, T_1 and of water at p_2, T_2 respectively, V_w the volume of water at D. The term $(p_1 - p_2)V_w$ represents the area FADE. The efficiency is

$$\frac{H_B - H_C}{H_B - H_D}.$$

The values of the total heat function are readily obtained from steam tables or charts which have been prepared for engineering work as explained in § 18.

It will be seen that the efficiency in Rankine's cycle is less than in Carnot cycle for in the former some heat (*viz.*, that required to heat the feed-water in the boiler from T_2 to T_1, is taken at a lower temperature. In actual steam engines the efficiency is only about 60—70% of the Rankine ideal and their indicator diagram resembles Fig. 12 with the corners rounded off.

18. Total heat of steam.—For calculating numerical values* it is usual to assume that the total heat or enthalpy of saturated water (*i.e.* water in equilibrium with its saturated vapour) at 0°C is zero and calculate the changes in total heat. Then the total heat of steam at θ°C is defined as the amount of heat required to convert 1 gram of water at 0°C into steam at θ °C. Regnault gave for the total heat of steam H the following empirical formula

$$H = 606{\cdot}5 + 0{\cdot}305\,\theta$$

where θ denotes the boiling point. The total heat may be computed as follows:

Let us raise the temperature of 1 gram of water from 0°C to its boiling point (t°C). Denoting the average specific heat at constant

* See Keesom and Keyes, *Thermodynamic Properties of Steam, including data on the liquid and solid phase*, (Wiley, 1936), or Callendar, *Steam Tables* (Arnold, 1936).

pressure by $\mathfrak{z}$, the heat required for this process will be $\mathfrak{z}t$ if we neglect* the small work done due to pressure changes. Thus the total heat of water at $t°$C is $\mathfrak{z}t$. Now let us evaporate this liquid at its boiling point $t°$. Consider the state of affairs when q gram of vapour has been produced leaving $(1-q)$ gram yet to be evaporated. Then q is called the *dryness fraction*. The volume of vapour produced is qv and the increase in volume is $q(v-w)$ where v is the specific volume of vapour at $t°$C and w the specific volume of water. Hence the external work done is $pq(v-w)$ in mechanical units. Therefore the gain in total heat during evaporation is

$$qL = qi + pq(v-w)$$

where i is the increase in internal energy when unit mass of the liquid is evaporated. Hence the total heat of steam at dryness fraction q is

$$H = \mathfrak{z}t + qL.$$

For dry saturated steam ($q = 1$), this becomes

$$H = \mathfrak{z}t + L.$$

If the dry saturated steam at $t°$C is further heated, its temperature rises and we now speak of it as superheated vapour. In the case of steam the superheating is usually produced under such conditions that we can assume that the superheating is carried out at constant pressure. Suppose the temperature of the superheated vapour to be t_1 °C so that there are $(t_1 - t)$ degrees of superheat. If c_p' be the mean specific heat of the vapour at constant pressure, the total heat of superheated vapour becomes

$$H_s = \mathfrak{z}t + L + c_p'(t_1 - t).$$

INTERNAL COMBUSTION ENGINES†

19. Historical Introduction.— Like other types of heat engines the idea of this type also dates from medieval times. Ch. Huygens,

* More rigorously

$$dH = d\,(u + pv) = du + pdv + vdp = Tds + vdp,$$

and $$\left(\frac{\partial H}{\partial T}\right)_p = c_p\,;\quad \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v = -T\left(\frac{\partial v}{\partial T}\right)_p + v$$

$$\therefore\quad dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

or $$\Delta H = \int_{T_0}^{T} c_p\,dT + \int_{p_0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

and we must integrate the right-hand side from 0°C (T_0°K) to the boiling point T and the pressure from the saturated vapour pressure p_0 at T_0 to the saturated vapour pressure p at T.

† These are called *internal* combustion engines because in them heat is produced by combustion of fuel *inside* the cylinder in contrast with the steam engine which may be called *external* combustion engine because in this case heat is produced in the boiler. The internal combustion engine is much more efficient than the steam engine because the working substance can be heated to a much higher temperature (2000°C.).

the great Dutch physicist, proposed in 1680 an engine consisting of a vertical cylinder and piston, in which the piston would be thrown upwards by the explosion of a charge of gunpowder. This would fill the cylinder with hot gases which would eventually cool, and the piston would be forced down by gravity. Each stroke would require a fresh charge of gunpowder.

This engine was never used, probably owing to the difficulty of introducing fuel after every explosion but the idea persisted. The discovery of combustible gases (coal gas, producer gas...) and of mineral oils brought the idea within the range of practical possibilities, as the difficulty of supplying fuel promised solution. But many long years of practical and theoretical study were necessary before such engines became commercially possible.

It is not possible to go into the details of these early attempts, and it will suffice to describe and explain the action of the two types* which have survived, *viz.*, (1) the Otto engine in which heat is absorbed at *constant volume*, (2) the Diesel engine in which heat is absorbed at *constant pressure*. Nearly 80 percent of internal combustion engines today are of the Otto type. We shall compare the action of these engines with that of the ideal Carnot engine in which heat is absorbed at *constant temperature*.

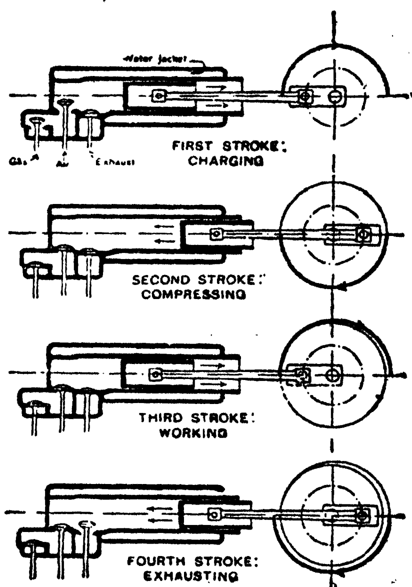


Fig. 13.—The four strokes of the Otto engine.

20. The Otto Cycle.—The Otto† cycle we are now going to describe was originally proposed by Beau de Rochas (1862), but the practical difficulties were first overcome by Otto in 1876. The working of the engine will be clear from Fig. 13. The engine consists of the cylinder and the piston, the cylinder being provided with inlet valves for air and gas (if gas is used for combustion), and exhaust valves. The opening and closing of these valves are controlled by the motion of the piston. There are four strokes in a complete cycle:

* Sometimes internal combustion engines are divided into (1) gas engine, (2) oil and petrol engines. It is, however, more scientific to divide them with regard to the cycles they follow and not with regard to fuel. Hence the engines have been divided into the constant volume, constant pressure and constant temperature type.

† Nikolaus Otto (1832-1891), born at Schlangenbad in Germany, is best known as the inventor of the four-stroke gas engine.

(*i*) *The Charging Stroke.*—In this the inlet valves are open, and a suitable mixture of air and gas is sucked into the cylinder by the forward motion of the piston.

(*ii*) *The Compression Stroke.*—During this stroke all the valves are closed, and the combustible mixture is compressed adiabatically to about 1/5th of its original volume by the backward motion of the piston. The temperature of the mixture is thereby raised to about 600°C.

At the end of the compression stroke, the mixture is fired by a series of sparks.

(*iii*) *The Working Stroke.*—The piston is now thrown forward with great force, since owing to combustion a large amount of heat is developed which raises the temperature of the gas to about 2000°C and a corresponding high pressure is developed.

(*iv*) *The Scavenging or the Exhaust Stroke.*—At the end of the third stroke, the cylinder is filed with a mixture of gases which is useless for further work. The exhaust valves are then opened, and the piston moves backward and forces the mixture out. After scavenging is complete, a fresh charge of gas and air is sucked in and a fresh cycle begins.

The thermodynamical behaviour is illustrated in the indicator diagram (Fig. 14).

It should be remembered that air is the working substance in the Otto engine, the function of gas or-petrol being merely to heat the air by its combustion. EC represents the suction stroke (gas and air being sucked at atmospheric pressure). CD represents the compression stroke. At D (pressure about 5 atmospheres, temperature about 600°C) the mixture is fired by a spark. A large amount of heat is liberated, and the representative point shifts to A (temperature 2000°C., pressure about 15 atmospheres), volume remaining constant. AB represents the working stroke. At B the exhaust valve is opened, and the pressure falls to the atmospheric pressure CV_1. CE is the scavenging stroke.

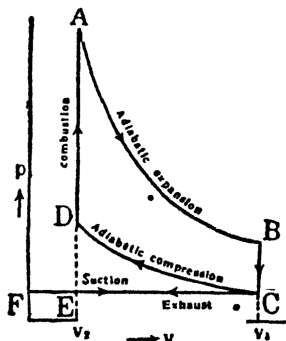


Fig. 14.—Four stroke Otto cycle.

The *efficiency* of the engine can be easily worked out. The amount of heat added $= C_v(T_a - T_d)$ where C_v is the specific heat at constant volume. (We suppose that this quantity retains the same value between 600°C., and 2000°C. which is only approximately true.)

$$\text{Heat rejected} = C_v\,(T_b - T_c).$$

$$\text{Hence efficiency } \eta = 1 - \frac{T_b - T_c}{T_a - T_d} \quad \ldots \quad (13)$$

From the relation $TV^{\gamma-1}$ = constant for an adiabatic (see p. 48, equation (24)), we obtain

$$\frac{T_a}{T_b} = \left(\frac{V_b}{V_a}\right)^{\gamma-1} = \frac{T_d}{T_c} = \rho^{\gamma-1} \quad \ldots \quad (14)$$

where ρ is the adiabatic expansion ratio. Hence

$$\frac{T_b - T_c}{T_a - T_d} = \left(\frac{1}{\rho}\right)^{\gamma-1}$$

Therefore the efficiency

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad \ldots \quad (15)$$

We obtain a similar expression for efficiency in terms of the adiabatic compression ratio as we get in a Carnot cycle (see equation 12, p. 216). The question arises: why not try to make the Carnot cycle a practical possibility ?

We shall now treat this question in more detail. In designing a machine, other factors have to be taken into consideration besides the mere question of theoretical efficiency. The engine must be, in the first place, quick-acting *i.e.*, a cycle ought to be completed as quickly as possible. This practically rules out the Carnot engine as it takes up heat at constant temperature, the process is therefore, very slow and the engine becomes very bulky and heavy in relation to the power output. In the Otto engine, the absorption of heat is almost instantaneous. But even where quickness is not the deciding factor, there are other weighty arguments against the adoption of the Carnot cycle. Pressure inside the cylinder varies during a cycle; and the machine must be so designed that it can withstand the maximum pressure. Hence practical considerations impose a second condition, *i.e.*, the maximum pressure developed inside the cylinder during a cycle should not be too great. Further, we must have a reasonable amount of work per cycle.

Now due to the adiabatic compression in the last stage of the Carnot cycle an enormous pressure is developed. A detailed consideration taking numerical values shows that working between the same two temperatures, say 2040°K and 340°K the Carnot engine develops a maximum pressure of about 1000 atm., while in the Otto engine it is only about 27 atm., though of course, the efficiency is reduced from 83% to about 44%. The Carnot engine also requires a large volume for the cylinder. These considerations show clearly that the Carnot engine is quite impracticable. It will have to be very bulky and very stout and the power output will be extremely small compared to its bulk.

In the case of the Diesel cycle which is described in the next section the maximum pressure developed is about 35 atm. and the efficiency rises to about 55%. It is for this reason that the Diesel engine is employed in cases where we want a large output of work.

21. Diesel Cycle.—Diesel* was dissatisfied with the low efficiency of the Otto engine and began investigations with the idea that the efficiency of the Carnot cycle may be reached by certain other contrivances. He did not succeed in his attempt, but was led to the invention of another engine which, for certain purposes, presents marked advantages over the Otto engine.

Now since

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$$

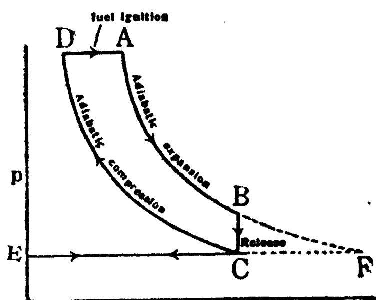


Fig. 15.—The Diesel cycle.

it is easily seen that if the compression ratio ρ can be still further pushed up, η would substantially increase. But in the Otto engine, ρ cannot be increased beyond a certain value (about 5) otherwise the mixture would be fired during compression before the spark passes.

In the Diesel engine no gas or petrol is introduced during compression. The indicator diagram for the cycle is shown in Fig. 15. In the first stage pure air is sucked in (EC in Fig.) and compressed to about one seventeenth of its volume (CD in fig.). A valve is then opened, and oil or vapour is forced under

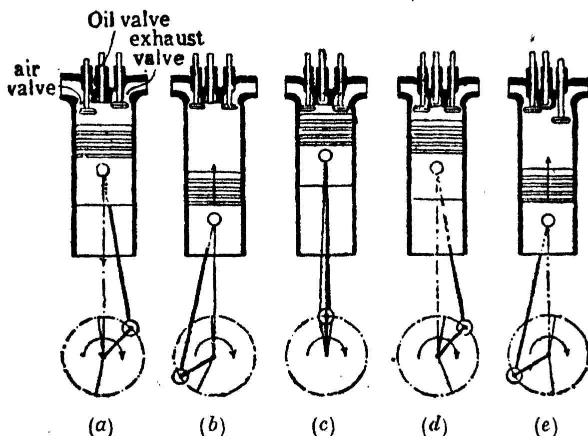


Fig. 16.—Strokes in a Diesel Engine.

(a) Beginning of suction stroke; air-valve open
(b) Beginning of compression stroke; all valves closed.
(c) Beginning of working stroke; oil valve open.
(d) Working stroke in progress. End of fuel injection; all valves closed.
(e) Beginning of scavenging stroke; exhaust valve open.

* Rudolf Diesel (1853-1913), born in Paris of German parentage, was the inventor of the heavy oil engine. He was engineer at Munich.

pressure. The oil burns spontaneously as the temperature in the cylinder is about 1000°C. and above the ignition point of the fuel. The supply of oil is so regulated that during combustion, as the piston moves forward, the pressure remains constant (DA). At a certain stage, when the temperature has reached the maximum value, about 2000°K, the supply of oil is cut off. The piston is allowed to move forward, describing the adiabatic AB. At B a valve is opened, and pressure drops to C. CE is the scavenging stroke in which the useless gas mixture is forced out, and the apparatus becomes ready for a fresh cycle.

The Diesel cycle can be performed in a cylinder of the type shown in Fig. 16. The cylinder is provided with the air inlet, the oil supply and the exhaust valves. The action of the cycle will be very clearly followed from the figure.

Instead of opening a valve at B we may allow the gas to expand as far as F where the inside pressure has fallen to atmospheric pressure, and the air mixed with the burnt gas be forced out by a back stroke FE. As this would involve a rather large volume for the cylinder, this procedure is not adopted in actual practice.

We shall now calculate the efficiency of the Diesel engine. Let us first calculate the efficiency for the imaginary cycle AFCD.

$$\text{Heat taken} = C_p(T_a - T_d).$$

$$\text{Heat rejected} = C_p(T_f - T_c).$$

From the relation $p = cT^{\gamma/(\gamma-1)}$ (equation 25, p. 48) we have

$$\left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma} = \frac{T_d}{T_c} = \frac{T_a}{T_f} = \frac{T_a - T_d}{T_f - T_c}$$

$$\therefore \quad \eta = 1 - \frac{T_f - T_c}{T_a - T_d} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

or

$$\eta = 1 - \left(\frac{p_2}{p_1}\right)^{(\gamma-1)/\gamma} = 1 - \left(\frac{V_a}{V_f}\right)^{\gamma-1}$$

$$= 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

So we have for the efficiency the same formula as for the Carnot or the Otto cycle. But in the Diesel engine the cylinder is designed for a maximum pressure of about 34 atmospheres. This determines the compression ratio because $p_1/p_c = \rho^\gamma = 34$. This gives $\rho = 12{\cdot}6$ and $\eta = 63\%$, which is a substantial improvement on the Otto engine.

But as stated above, we have to take the cycle DABC. Heat is rejected at constant volume. Hence heat rejected is equal to

$$C_v(T_b - T_c).$$

$$\therefore \quad \eta = 1 - \frac{C_v(T_b - T_c)}{C_p(T_a - T_d)} \quad . \quad . \quad . \quad . \quad (18)$$

which yields a lower value of about 55%.

The Diesel engine, therefore, consumes less fuel than the Otto engine, but as it has to withstand a higher pressure it must be more robust. Also the mechanical difficulties are much greater, but they have been successfully overcome.

22. Semi-Diesel Engines.— We have seen that in Diesel engines a large compression ratio (17 to 1) is employed and the maximum pressure developed is enormous (35 atm.) ; further, a costly high pressure air blast is necessary to force the liquid fuel into the cylinder. To avoid these the Semi-Diesel engine, also called the ***hot-bulb engine***, has been invented. In this air is compressed to about 15 to 20 atm. instead of 35 atm. This air does not yet become hot enough to ignite the oil and is consequently passed through a hot bulb where it is heated by contact with the bulb to the required temperature. The hot bulb is simply a portion of the cylinder which is not cooled by the water jacket. It consequently becomes much heated and serves to heat the compressed air. Next the oil (fuel) is injected into this hot bulb where, by the combined action of the compressed air and the hot bulb, it ignites. For starting the machine the hot bulb must be heated by a separate flame. After a few cycles the bulb becomes hot and begins to function properly. Then the external flame is removed. The semi-Diesel engines now-a-days are generally two-stroke oil engines without automatic control valves.

23. The "National" Gas Engine.—We shall now describe a typical Otto engine. Fig. 17 shows a 100 horse-power "National" gas engine.

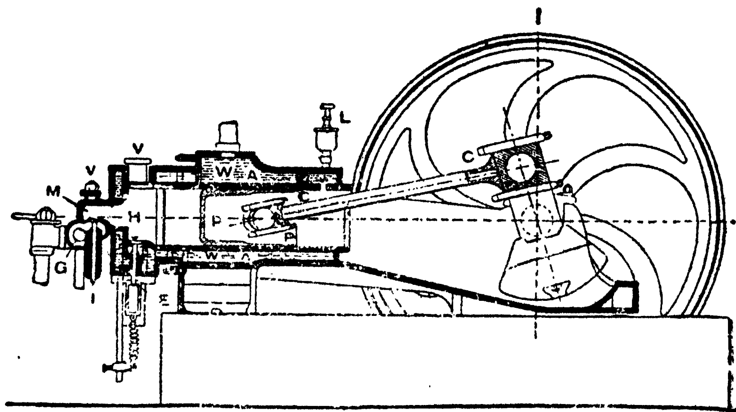


Fig. 17.—The "National" gas engine.

The engine is a stationary horizontal one having a single cylinder AA. The piston PP is attached to the crank shaft by the connecting rod CC and fits gas-tight into the cylinder AA. H is the combustion chamber having the inlet valve I, the gas valve G and the exhaust valve E. The cylinder, the combustion chamber and the valve casings are cooled by the water jacket WW. L is the lubricator, V, V are plugs which may be removed in order to examine the valves. M is

the ignition plug where a spark is produced by the "Magneto" and serves to ignite the charge. The various valves and the magneto are worked by suitable cams mounted on a shaft driven by the crank shaft.

The working of the machine is identical with that indicated in Fig. 13. The machine is started by rotating the fly-wheel so that the piston commences its outward stroke. An explosive mixture is introduced and ignited and the piston is thrown forward. Then the working follows as indicated on p. 223.

24. Diesel Four-Stroke Engines.— These engines employ a cylinder and valves of the type shown in Fig. 16. In constructional design they are not much different from the Otto engine. They are further provided with a high pressure air blast for injecting the liquid fuel.

25. The Fuel.— Some engines employ gaseous fuels the chief of which are coal gas, producer gas, coke-oven gas, blast-furnace gas, water gas and natural gas (chiefly methane). The common liquid fuels are petrol, kerosene oil, crude oil, benzol and alcohol. In the Otto engine, if liquid fuel is used, it must be first vaporised and then admitted. Diesel engines generally employ crude oils and hence their fuel is very cheap.

26. Applications.—During the brief period of fifty years the internal combustion engines have been much developed and employed for a variety of purposes. The steam engine, we have seen, is very wasteful of fuel, but the internal combustion engine is much more economical and has consequently been widely employed.

The Otto four-stroke engine is usually employed in motor cars and aeroplanes. Petrol vapour is used as fuel in both cases. Four-stroke Diesel engines are largely employed in driving ships. Where very large power is necessary, the two-stroke Diesels are in common use. Diesel engine is more efficient and more economical of fuel. Still has combined a steam engine with a Diesel engine and has obtained much greater efficiency in steam locomotives (Still-Kitson locomotives.)

STEAM TURBINES

27. The Steam Turbine.— We shall now give a brief description of the engines belonging to the windmill type. Windmills are set in motion by the impact of wind on the vanes of the mill, and at first sight it may appear strange why they would be classed as heat engines. But a little reflection will show that the wind itself is due to the unequal heating of different parts of the earth's surface, hence the designation is justified. But wind-power is rather unreliable, hence steam turbines were invented in which the motive power is supplied by the artificial wind caused by high pressure steam. There are two types of turbines:—(1) *The Impulse Turbine* in which steam issuing with great velocity from properly designed nozzles strikes against the blades set on a turbine wheel and in passing through them

has its velocity altered in direction. This gives an impulse to the wheel which is thereby set in rotation. (2) *The Reaction Turbine* is somewhat similar in principle to the Barker's Mill which, as a laboratory toy, has been known to generations of students. In this the wheel is set in rotation in the opposite direction by the reaction produced by a jet of steam issuing out of the blades set in the wheel.

Though the steam turbines are simple in theory, in practice great mechanical and constructional difficulties had to be encountered, but thanks largely to the efforts of De Laval, Curtis and most of all to Sir Charles Parsons who may be described as the James Watt of the steam turbine, these difficulties were successfully overcome. To-day the turbine is a prime mover of great importance and is almost exclusively used as the source of power for all large power land stations for the generation of electricity and propulsion of big ships. Their great advantage lies in the fact that instead of the reciprocating motion of the ordinary steam engine, a uniform rotary motion is produced by a constant torque applied directly to the shaft. They are more efficient than other engines because there is no periodic change of temperature in any of their parts and hence no heat is wasted. The full expansive power of steam can be utilised under suitable conditions.

28. The Theory of Steam Jets.— The essential feature of the turbines is that in them the heat energy of steam is first employed to set the steam itself in motion inside the fixed nozzles or bladings (in reaction turbines) and this kinetic energy is utilised in doing work on the blades. The fixed nozzles are so designed as to convert most efficiently the thermal energy of steam into its kinetic energy and produce a constant jet. We shall, therefore, first study the formation of jet under these conditions. We shall derive an expression for the kinetic energy imparted to the steam in traversing the fixed nozzle from the region of high pressure B (Fig. 18) to the region of low pressure C.

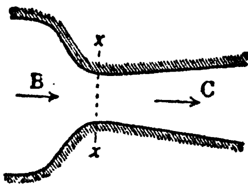


Fig. 18.—The fixed nozzle producing the jet.

Let the pressure, volume, internal energy and velocity of steam in B per gram be denoted by p_1, v_1, u_1 and w_1 and the corresponding quantities in C by p_2, v_2, u_2 and w_2. Then the gain in kinetic energy of steam per gram on traversing the nozzle is $(w_2^2 - w_1^2)/2J$ calories. The net work done on steam in this process as on p. 138 is $p_1v_1 - p_2v_2$ while the loss in internal energy is $u_1 - u_2$. Thus on the assumption that the process is adiabatic we have from the first law of thermodynamics,

$$\frac{1}{2J}(w_2^2 - w_1^2) = p_1v_1 - p_2v_2 + u_1 - u_2 = h_1 - h_2, \quad . \quad . \quad (19)$$

i.e., the gain in kinetic energy is equal to the heat drop. Generally the initial velocity is sensibly zero and hence the kinetic energy of the issuing jet is given by the heat drop $h_1 - h_2$.

If we now assume that there is no loss of heat energy through friction or eddy currents in the nozzle, the heat drop $h_1 - h_2$ is equal to the heat drop from the pressure p_1 to p_2 under isentropic conditions. This can be readily obtained from steam tables and represents under most favourable conditions the maximum work obtainable from the turbine. Under ideal conditions the ordinary steam engine would also yield the same amount of work, *i.e.*, equal to the heat drop. The greater efficiency of steam turbines is, however, mainly due to the following two causes:—(1) in the turbine there are nowhere any periodic changes in temperature as are found in the cylinder of the steam engine ; (2) the turbine is capable of utilising low-pressure steam with full advantage.

29. The De Laval Turbine.—The velocity which is theoretically attainable in a steam jet is, therefore, enormous, and this causes extraordinary mechanical difficulties. For if we want to utilise the whole of this energy, by allowing the jet of steam to impinge on the blades or buckets of a turbine wheel, simple mathematical considerations show that the velocity of the blades should not be short of one-half the velocity of the jet. Thus for maximum efficiency we should have a speed of the order of 100 metres/sec. at the periphery of the wheel which carries the blades. The number of revolutions per minute necessary to produce such peripheral speeds for a wheel of moderate dimensions reaches the value of about 30,000 and such speeds are impracticable for two reasons. First, there are no constructional materials which can withstand such enormous peripheral speeds. The rotating parts would fly to pieces on account of the large centrifugal forces developed and there would be mechanical vibration of the rotating shaft. Secondly, if the shaft is to be coupled to another machine which should usually rotate at a much lower speed, say, 2000 r.p.m., the problems of gearing become almost insuperable. These difficulties were first successfully overcome by De Laval for low-power turbines. For the gearing down, he used double-helical gear wheels with teeth of specially fine pitch. To enable the requisite peripheral speeds to be obtained with safety, the turbine wheel was made very thick in the neighbourhood of the axis (see Fig. 19) so that it can withstand the stresses set up by rotation and further the shaft was made thin.

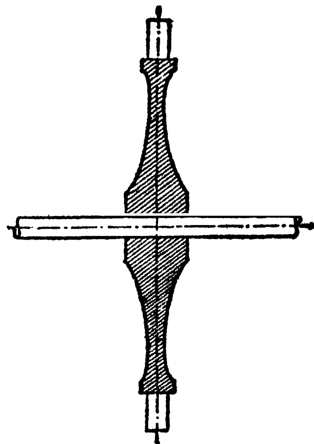


Fig. 19.—Vertical section of the wheel of De Laval turbine.

A De Laval turbine is illustrated in Fig. 20. The steam jet issuing from the fixed nozzles impinges on the blades, has its direction

changed by them and thereafter escapes to the exhaust. Due to this action of the steam the blades are set in rotation. These are known as '*impulse turbines*' because the steam in passing through them is not accelerated but has only its direction changed. The interaction of steam with the blades is clearly indicated in Fig. 21. In these turbines the blades are 'parallel,' i.e., a passage between two blades has nearly the same cross-section everywhere so that the blades offer very little obstruction to the steam jet and hence the pressure of the steam remains practically the same on both sides of the wheel.

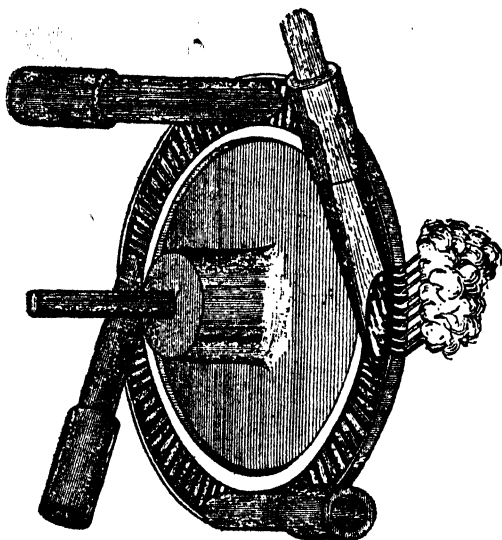


Fig. 20—A De Laval turbine.

30. Division of the Pressure Drop into Stages. Rateau and Zolly Turbines.— As a prime mover, the De Laval turbine is quite efficient for producing low power. For generating high power, superheated steam must be used so that the pressure drop in the jet would be enormous, and hence for maximum efficiency the blades must move with very high velocity. Such large velocities are incompatible with safety. For this reason, the entire pressure drop is divided into a number of stages. Each stage consists of one set of nozzles and one ring of moving blades mounted on a wheel fixed to the shaft. Across each stage, the pressure drop is small, so that the blade velocity necessary for maximum efficiency is considerably reduced and can be easily attained in practice. This principle of *pressure compounding* was first given by Parsons and later adopted by Curtis, Rateau and Zölly to the De Laval type. Rateau turbine has 20 to 30 stages, Zölly has about 10.

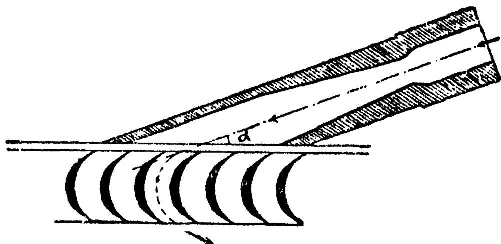


Fig. 21.—Action of steam on the blades of a De Laval turbine.

31. Reaction Turbines—Parsons' Work.— Parsons* began his researches on steam turbine about the same time as De Laval (1884), but he did not accept the latter's solution of the problem, and went on with his own investigations which were completed by about 1897. His researches resulted in the evolution of a completely new type—the so-called *Reaction Turbines.* The mechanism of this type is shown in Fig. 22.

The essential feature of the Parsons' turbine is its blading system. This consists of alternate rings of a set of fixed blades mounted on the inside of the cylindrical case or the stator, with a set of moving blades mounted on the shaft or the rotor, arranged between each pair of rings of fixed blades as shown in Fig. 22. There are no separate nozzles for producing a jet, but the fixed blades act as nozzles. It will be noticed that the blades have convergent passages, *i.e.*, the cross-section of the passage goes on decreasing towards the exit side.

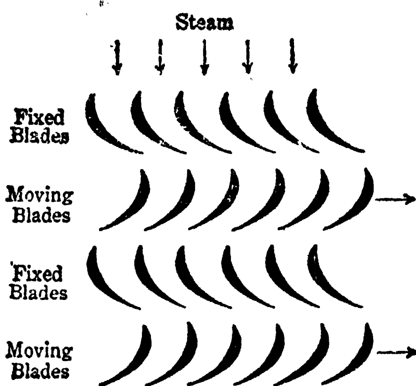


Fig. 22.—The blading system of a reaction turbine.

As the steam passes through the moving blades, there is a drop of pressure in consequence of which the steam jet increases in velocity as it traverses the blade-passage, and as it issues out, a backward *reaction* is produced on the blades which consequently begin to revolve. The steam then again passes to the next set of fixed blades where it again acquires velocity and enters the next set of moving blades nearly perpendicularly.

The moving blades are secured in grooves on the rotor shaft with their lengths radially outwards and parallel to each other. The fixed blades are secured in grooves in the enclosing cylinder and project inwards almost touching the surface of the spindle. The steam is admitted parallel to the axis of the shaft (axial flow type). One pair of rings of moving and fixed blades is said to form a *stage*, and generally a turbine has a large number of stages.

Pressure Compounding.—On account of the peculiar form of the blade-passages, the pressure goes on falling rather slowly, so that the whole pressure drop is spread over a large number of stages which may amount to 45 or even 100. In consequence of this arrangement the velocity of the jet is very small compared to that of the De Laval type and the requisite blade speed is 100 to 300 ft. per sec.

* Charles Algernon Parsons (1854-1931) built the first reaction turbine in 1886 at Newcastle-on-Tyne. He was awarded the Copley & the Rumford medals of the Royal Society for his inventions.

This reduction of velocity brought about by the distribution of available pressure over a large number of stages constituted the master-invention of Parsons which was also applied to other turbines with great advantage as already mentioned.

We have stated above that the steam enters the moving blades perpendicularly. In actual practice, however, the steam enters the moving blades with some relative velocity giving it an impulse as in De Laval's turbine and so the turbine works partly by impulse and partly by reaction. Thus it will be seen that the distinction between 'impulse' and 'reaction' turbines is more popular than scientific and should not be taken too literally. All turbines are driven by 'reaction,' due to the alteration of velocity of the steam jet in magnitude and direction. The real distinction between the two types is that in the 'impulse' turbines the reaction is due to the steam jet being slowed down while in the pure 'reaction' turbine the reaction is produced by the acceleration imparted to the steam in the moving blades themselves on account of the pressure drop. Still, however, by simply looking at the blades one can say whether the turbine is of the 'impulse' or 'reaction' type, the impulse blading being characterised by parallel passages and the reaction blading by the convergent passages.

During the last thirty years high-pressure gases have been utilised in place of steam to drive the blades of a turbine. In the internal combustion gas turbine the combustion of some oil serves to heat the enclosed air to a high temperature and high pressure, and this high pressure gas drives the turbine wheel.

32. Alternative types of Engines.— During the Second World War the *jet propulsion system* was developed in Germany and Italy mainly with the idea of devising a powerful means of propulsion for high-speed aircraft. In a modern *turbo-jet* a mixture of air and fuel is sucked in and compressed by a compressor and then ignited so as to generate high pressure. This high pressure gas traverses a turbine where it gets accelerated and the pressure falls, the gas escaping at the rear of the machine with a high jet velocity. The machine on account of the reaction thus furnished, moves forward with tremendous velocity. In this way the modern jet plane has been able to attain supersonic velocities *i.e.* velocities greater than the velocity of sound.

Mention may be made of the Rocket and the guided missile whose use by the Germans in World War II as V-2 rocket caught world imagination and whose potentialities for space travel are bound to make it an important tool of the future for scientific research. The essential difference between a rocket and a jet aircraft is that the former carries its own oxygen supply and thus can operate in vacuum while the latter obtains oxygen from the air. The propellant, solid or liquid, ignites producing a jet and the rocket takes off. The final rocket velocity $V_r = w \log_e M^*$ where w is the jet velocity and M^* denotes the ratio of the initial mass of the rocket to the final mass after combustion. In the two-stage rocket a smaller second

rocket is placed in the nose which ignites a few minutes after take-off and the second rocket detaches itself and forges ahead under its own power with a tremendous velocity. Such a multi-stage rocket was used by the Russians to launch the first artificial earth satellite on 4th October, 1957 and the first artificial planet on 2nd January, 1959. The thrust developed by these rockets is enormous.

THERMODYNAMICS OF REFRIGERATION

33. In Chapter VI we described several refrigerating machines and considered the general principles upon which their action depends. We shall now investigate the problem of the efficiency of these machines. In order to compare the efficiency of the various machines we shall introduce a quantity called the *coefficient of performance* of a refrigerating machine. If by the expenditure of work W a body is deprived of its heat by an amount q, its coefficient of performance is given by q/W.

In Section 15 we saw that if a Carnot engine with a perfect gas as the working substance is worked backwards between the source of heat at T_1 and the condenser at T_2, the working substance abstracts an amount of heat Q_2 from the condenser and yields Q_1 to the source where Q_1 and Q_2 are connected by the relation $Q_1/T_1 = Q_2/T_2$. The work done in driving the engine is $Q_1 - Q_2$. Hence the coefficient of performance of a Carnot engine working as a refrigerating machine is

$$\frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}. \qquad (20)$$

It can now be easily proved much in the same way as on p. 219 *that no refrigerating machine can have a coefficient of performance greater than that of a perfectly reversible machine working between the same two temperatures, and that all reversible refrigerating machines working between the same temperatures have the same coefficient of performance.* It thus follows that the coefficient of performance of any perfectly reversible refrigerating machine working between temperatures T_1 and T_2, whatever the nature of the working substance, is equal to $T_2/(T_1 - T_2)$, and this is the maximum possible.

A Carnot engine using perfect gas and working backwards will be a most efficient refrigerating machine but its output will be small due to the small specific heat of gases. For large capacity we must employ a liquid of large latent heat of vaporization and allow it to evaporate at the lower temperature. We have seen in §6, p. 128 how practical considerations have led us to select ammonia and a few other substances for this purpose.

34. Efficiency of a Vapour Compression Machine.—We shall now calculate the efficiency of the vapour compression machine

described on p. 127. Let us trace the cycle of changes which the working substance undergoes. For this purpose assume the valve V to be replaced by an expansion cylinder. AB (Fig. 23) represents the evaporation of the liquid in the refrigerator, BC the adiabatic compression of the vapour by the compressor, CD the liquefaction of the substance inside the condenser and DA the adiabatic expansion of the liquid in the expansion chamber (not shown). The cycle ABCD is perfectly reversible and hence its coefficient of performance is given by equation (20).

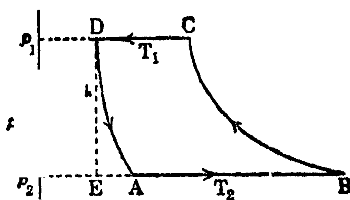


Fig. 23.—Cycle of a vapour compression machine.

In actual machines the throttle valve takes the place of the expansion cylinder. This is done for mechanical simplicity. Consequently the part DA of the ideal cycle is replaced by DEA. On account of the irreversible expansion through the valve there is a loss of efficiency. The losses are twofold. An amount of work equal to the area DEA is lost and there is also reduced refrigeration effect since some liquid evaporates before reaching the refrigerator. The coefficient of performance for the actual machine can be calculated as in the case of Rankine's cycle (p. 220) from the values of the total heat of the working substance in the different states.

Books Recommended.

1. *Andrade*, Engines.

2. Ewing, *Steam Engine and other Heat Engines.*

3. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, Articles on Steam Engine; Engines, Thermodynamics of Internal Combustion; Turbines, Development of; Turbines, Physics of.

4. Judge, *Handbook of Aircraft Engines* (1945), Chapman & Hall Ltd.

5. Clarke, *Interplanetary Flight* (1952), Temple Press Ltd., London.

CHAPTER X

THERMODYNAMICS

1. Scope of Thermodynamics.— The object of the science of Heat is the study of all natural phenomena in which heat plays the leading part. We have hitherto studied a few of these phenomena in a detached way, *viz.*, properties of gases, change of state, variation of heat content of a body (calorimetry). There are other phenomena (*e.g.*, Radiation, i.e., the production of light by heated bodies) which have not yet been treated; there are others which, strictly speaking, do not come under physics, *viz.*, Chemical equilibria, Electro-chemistry, but in which heat plays a very prominent part. The detailed study of all these phenomena is beyond the scope of this volume. The object of this chapter is simply to develop general methods for the study of all such phenomena.

The first requisite for such studies is the *definition of the thermal state of a body or system of bodies.* Next comes the development of general principles. The studies fall under two headings—(i) the study of energy relationships, (*ii*) the study of the direction in which changes take place. The guiding principles for the two cases are the First and the Second Laws of Thermodynamics.

2. The Thermal State of a Body or System of Bodies.— The thermal state of a simple homogeneous body like a gas or a solid is defined by its temperature T, pressure p or the volume V. These quantities are, therefore, called *Thermodynamical Variables*. Of the three quantities only two are independent, the third being automatically fixed by the value of the first two, for it is a common observation that the pressure, volume or temperature of a substance in any state, solid, liquid or gas, is perfectly definite when the other two quantities are known. Hence for every substance the pressure, volume and temperature are connected by a relation of the form

$$p = f\ (v,\ T). \qquad . \quad . \quad . \quad . \qquad (1)$$

This is called the 'Equation of State' of the substance. The form of (1) is known only for a perfect gas (Chap. IV). But though (1) is generally unknown we can proceed a good deal towards studying the behaviour of a substance under different conditions by using differential expressions. In the subsequent work we shall occasionally use differential calculus and some of its important theorems. The reader must clearly understand the physical interpretation of these and for that purpose the following brief mathematical notes are appended.

3. Mathematical Notes.— Suppose that y is some function of the variable x and is continuous over a certain range of x. Let δx be some increment in the value of x and let δy be the corresponding

increment of y, such that $y+\delta y$ still lies within the range of y continuous. Then the value of the ratio $\frac{\delta y}{\delta x}$ as δx tends to zero is the differential coefficient of y with respect to x and is written $\frac{dy}{dx}$.

If x is a function of the two variables y and z, *i.e.*,

$$x = f\ (y,\ z), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

there are two differential coefficients of the function. In the first case the function may be differentiated with respect to y keeping z constant, and in the second it may be differentiated with respect to z keeping y constant. These differential coefficients are known as partial differential coefficients and are written

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial f}{\partial y}\right)_z \quad \text{and} \quad \left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial f}{\partial z}\right)_y$$

where the suffix outside the bracket denotes the variable which is kept constant during differentiation.

In order to find the variation in the quantity x when y and z are both increased by the amounts δy and δz we must make a double application of Taylor's theorem. Now if $x = f(y)$ we have from Taylor's theorem

$$x+\delta x = f(y+\delta y) = f(y)+\delta y\frac{df}{dy} + \frac{(\delta y)^2}{2!}\cdot\frac{d^2f}{dy^2} + \quad . \quad . \quad .$$

When x is a function of the two variables y and z, the value of $f(y+\delta y,\ z+\delta z)$ may be obtained by first considering the second variable constant at $z+\delta z$ and expanding in terms of δy only by Taylor's theorem. In the second stage y is kept constant and the terms which are functions of $z+\delta z$ are expanded by Taylor's theorem in terms of δz. Let us denote the partial derivative of $f(y,\ z)$ with respect to y by f_y and so on. Hence

$$\begin{aligned} x+\delta x &= f(y+\delta y,\ z+\delta z) \\ &= f(y,\ z+\delta z) + \delta y\ .f_y(y,\ z+\delta z) \\ &\quad + \tfrac{1}{2}(\delta y)^2.\ f_{yy}(y,\ z+\delta z) + \text{higher terms in } \delta y. \end{aligned}$$

Expanding each term on the right-hand side by Taylor's theorem in terms of δz we obatin

$$\begin{aligned} x+\delta x &= f(y,\ z) + \delta y.f_y(y,\ z)+\delta z.f_z(y,\ z) \\ &\quad + \tfrac{1}{2}\{(\delta y)^2.f_{yy}(y,\ z) + 2\delta y.\delta z.f_{yz}(y,\ z) + (\delta z)^2.f_{zz}(y,\ z)\} + . \ . \ . \quad (3) \end{aligned}$$

If instead of expanding first in terms of δy, we had expanded first in terms of δz and then in terms of δy we would have obtained an expression similar to (3) with the only difference that instead of $f_{yz}(y,\ z)$ we would now obtain $f_{zy}\ (y,\ z)$. Since these two values of $x+\delta x$ must be identical we have

$$f_{yz}(y, z) = f_{zy}(y, z).$$

or
$$\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

i.e., the order in which the differentiation is performed is immaterial.

If the variations δy, δz are continuously decreased so that the terms involving their higher powers may be neglected, equation (3) reduces to the form

$$x + \delta x = x + \delta y \cdot f_y + \delta z \cdot f_z$$

or
$$\delta x = \left(\frac{\partial x}{\partial y}\right)_z \delta y + \left(\frac{\partial x}{\partial z}\right)_y \delta z \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This is the theorem of partial differentiation.

Let us consider the equation

$$\delta x = M\delta y + N\delta z. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

On comparison with (5) we see that if equation (6) is obtained from an equation of the form (2) we should have

$$M = \left(\frac{\partial x}{\partial y}\right)_z; \quad N = \left(\frac{\partial x}{\partial z}\right)_y. \quad (7)$$

Conversely, if M and N are of this form there must exist a functional relation of the form (2) connecting the variables y and z. When (2) exists condition (4) is satisfied which from (7) is equivalent to the condition

$$\frac{\partial M}{\partial z} = \frac{\partial N}{\partial y}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Hence if condition (8) exists, equation (6) must result from an equation of the form (2). Then δx is said to be a perfect differential. The physical meaning of this is that the change in x for the change in the variables y and z from y_1, z_1 to y_2, z_2 is given by

$$x_1 - x_2 = f(y_1, z_1) - f(y_2, z_2),$$

and is consequently independent of the path of transformation, depending only upon the initial and final values of the variables.

There exist some physical processes for which a relation of the type (6) exists but (8) is not satisfied. Then δx is not a perfect differential. As a mathematical example consider the expression

$$\delta x = 3yz\,dy + 2y^2dz. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Then
$$\frac{\partial x}{\partial y} = 3yz; \ \frac{\partial x}{\partial z} = 2y^2$$

$$\frac{\partial^2 x}{\partial z \partial y} = 3y; \ \frac{\partial^2 x}{\partial y \partial z} = 4y.$$

$$\therefore \quad \frac{\partial^2 x}{\partial y \partial z} \neq \frac{\partial^2 x}{\partial z \partial y} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Hence (9) cannot be integrated as can be easily verified. The condition of integrability is just the reverse of (10). If we multiply (9) by yz the resulting function $3y^2z^2dy+2y^3zdz = d(y^3z^2)$ is integrable. The quantity yz is called the integrating factor of the expression δx.

In equation (5), suppose z is kept constant, *i.e.*, $\delta z=0$. Then, on division by δx, we obtain

$$1 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z$$

or

$$\left(\frac{\partial x}{\partial y}\right)_z = 1 \Bigg/ \left(\frac{\partial y}{\partial x}\right)_z \qquad . \quad . \quad . \quad . \quad (11)$$

which implies that the reciprocal of the partial differential coefficient is equal to the inverted coefficient.

4. Some Physical Applications.— From equation (1) we have, on differentiation, in the general case

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT. \qquad . \quad . \quad . \quad (12)$$

For an *isobaric* or *isopiestic process*, $dp=0$. Hence equation (12) yields

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p. \qquad . \quad . \quad . \quad (13)$$

Now $\quad \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_p$ = coefficient of volume expansion in an isobaric process (Chap. VII).

$-v\left(\dfrac{\partial p}{\partial v}\right)_T$ = bulk modulus of elasticity in an isothermal process, or inverse of the coefficient of compressibility.

$\dfrac{1}{p}\left(\dfrac{\partial p}{\partial T}\right)_v$ = coefficient of pressure increase in an isochoric (constant volume) process.

Equation (13) shows that the volume elasticity, the volume coefficient of expansion and the pressure coefficient of expansion are not independent but are inter-related.

As an illustration, consider mercury at 0°C. and under atmospheric pressure. The coefficient of volume expansion is $1{\cdot}81\times10^{-4}$ per °C. and the coefficient of compressibility per atmosphere is $3{\cdot}9\times10^{-6}$. Hence from (13)

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_p}{-\dfrac{1}{v}\left(\dfrac{\partial v}{\partial p}\right)_T} = \frac{1{\cdot}81\times10^{-4}}{3{\cdot}9\times10^{-6}} = 46{\cdot}5 \text{ atm.}$$

and the pressure coefficient

$$\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v = 46{\cdot}5.$$

Hence it follows that a pressure of about 46 atm. is required to keep the volume of mercury constant when its temperature is raised from 0°C. to 1°C. Thus if the capillary tube of a mercury thermometer is just filled with mercury at 30°C., the pressure exerted in the capillary when it is heated to 34°C. will become $4 \times 46{\cdot}5 = 186$ atmospheres.

5. Different Forms of Energy.— As thermodynamics is largely a study of energy-relationships, we must clearly understand the term '*Energy*'. The student must be familiar with the concept of 'Energy' from his study of mechanics. 'Energy' of a body may be defined as its capacity for doing work and is measured in ergs on the C.G.S. system of units.

Everybody must be familiar with the two ordinary forms of energy, *viz.*, the *kinetic energy* and the *potential energy*. A revolving fly-wheel possesses a large amount of kinetic energy which can be utilised in raising a piece of stone from the ground, *i.e.*, in doing work. In this process the kinetic energy of the flywheel is converted into the potential energy of the mass of stone. The mass of stone also in its raised level possesses energy which we call potential energy and which can also be made to yield work. For when the stone falls down under gravity the flywheel can be coupled to a machine and be made to do work. Thus kinetic and potential energies are mutually convertible and in a conservative system of forces the sum of the kinetic and potential energies is constant throughout the process. All moving bodies possess kinetic energy by virtue of their motion and all bodies placed at a distance from a centre of force possess potential energy by virtue of their position.

There are other forms of energy also with which the student of physics must have become familiar, and which we shall now take up. We have already pointed out that *heat* consists in the motion of molecules and must therefore be a form of energy. The experiments of Joule and Rowland showed that there exists an exact proportionality between mechanical energy spent and the heat developed. Friction is the chief method of converting mechanical energy into heat. The conversion of heat into work has also been accomplished by the help of steam engines and other heat engines which have been completely described in Chap. IX. Thus it has been fully established that heat is a form of energy.

Energy may be manifested in *electrical* phenomena also in a variety of ways. It is well known that when two current-carrying coils are placed with their planes parallel to each other, they attract or repel each other depending upon the direction of flow of the current. In this case we may take the more familiar example of the tramway. Here electric currents are made to run the carriage. Again a wire

carrying a current becomes heated. Thus electricity is also a form of energy which can be easily converted into mechanical or thermal form.

Energy may also be manifested as *chemical energy*. For we know that a bullet fired from a gun possesses enormous kinetic energy which is derived from the chemical actions that take place when the powder detonates. Further a large amount of heat is evolved during a number of chemical reactions, *viz.*, in the combination of hydrogen and oxygen. Also the chemical actions going on in a voltaic cell produce electrical current. Thus chemical energy can be easily converted into mechanical energy, heat, electrical energy, etc.

There are various other forms of energy, all of which can be converted into some one of the other forms. The important ones are the following:—magnetic energy, radiant energy (Chap. XI), surface energy (surface tension), radioactive energy and energy of gravitation.

There are three important laws governing energy transformation:—(1) *The Transmutation of Energy*, (2) *The Conservation of Energy*, (3) *The Degradation of Energy*.

6. The Transmutation of Energy.— This principle states that energy can be converted from one form to another. We have already seen how mechanical energy, electrical energy and chemical energy can be converted into heat. In fact all kinds of energy can be directly converted into heat. Mechanical energy obtained from a water-fall working a turbine, may be utilised to generate electrical energy by coupling the turbine to a dynamo. Electrical energy may be converted into thermal energy as in electrical furnaces, or into chemical energy as in the charging of secondary cells. Heat energy can be converted into electrical energy as in the phenomena of thermo-electricity, into mechanical energy as in steam engines, and so on. Examples could be multiplied indefinitely.

7. The Conservation of Energy.— The principle states that during a process involving interchanges of energy, the total energy of the system remains constant. In other words energy is indestructible and uncreatable by any process. No formal proof of the law can be given. It is a generalisation based upon human experience and is amply borne out by its consequences. The law arose out of the attempts of earlier philosophers to devise a machine which will do work without expenditure of energy. They however failed in their attempt. Later it was recognized that all the machines invented were simply devices to multiply force and could not multiply energy, and the true function of a machine was to transmit work. Only that much work could be obtained from a machine as was supplied to it, and that too in ideal cases. This shows that energy obeys the law of conservation. In these cases, however, all energy cannot be recovered as some is dissipated as heat. But heat is also a form of energy, and on equating the work obtained plus the heat developed to the work done, we find that the relation of equality is satisfied. Thus the principle is established for this case and follows from a result of human experience which may be stated in this form:—

"It is impossible to design a machine which will create energy out of nothing and produce perpetual motion. Energy can only be transformed from one form to another."

8. The Dissipation of Energy.—Energy, we have seen, is capable of existing in different forms. In some forms however it is more available to us than in other forms, *i.e.*, we can get more work from energy in one form than in another. For example, mechanical energy is the highest available form while the heat energy of a body at a low temperature is in a much less available form. Now the law of degradation or dissipation of energy says that *energy always tends to pass from a more available to a less available form. This is called the degradation or dissipation of energy*, and is intimately connected with the Second Law of Thermodynamics; it will therefore be taken up later.

FIRST LAW OF THERMODYNAMICS

9. The First Law.— We have already enunciated the law of conservation of energy. The First Law of Thermodynamics is simply a particular case of this general principle when one of the forms of energy is heat. It may be mathematically stated in the form*

$$\delta Q = \delta U + \delta W, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where δQ is the heat absorbed by the system, δU the increase in its internal energy and δW the amount of external work done by it. It may be remarked that δQ is here expressed in energy units, and can be found by multiplying the heat added in calories by J, the mechanical equivalent of heat. For a simple gas expanding against an external pressure p, $\delta W = p\delta V$, but for surfaces, magnetic bodies, etc., other suitable terms are to be added to take into account other forms of energy such as mechanical, electrical, etc. The quantity 'internal energy' is defined with the help of the principle of conservation of energy by considering a thermally insulated system for which $\delta U = -\delta W$. Changes in internal energy can thus be measured in terms of the external work done on the system.

APPLICATIONS OF THE FIRST LAW

10. Specific Heat of a Body.—It is easy to see that the internal energy of a body or a thermodynamical system depends entirely on its thermal state and is uniquely given by the independent thermodynamical coordinates. In the case of a simple homogeneous body we have seen on p. 237 that any two of the variables p, v, T are sufficient to define its state uniquely. Choosing therefore V and T as independent variables we have

$$U = f(V, T), \quad . \quad . \quad . \quad . \quad . \quad (15)$$

* It was first stated in this form by Clausius.

where U and V refer to a gram-molecule of the substance. Differentiating (15) we get*

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \quad . \quad . \quad . \quad (16)$$

For a perfect gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (p. 47) ; for a gas obeying van der Waals' equation (see §33)

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}.$$

If an amount of heat δQ be added to a thermodynamical system, say a perfect gas, part of it goes to increase the internal energy of the gas by dU, while the remainder is spent in doing external work, e.g., when the gas expands by a volume dV against the pressure p. We have from the first law,

$$\delta Q = dU + pdV, \quad . \quad . \quad . \quad . \quad (17)$$

where δQ, dU are expressed in energy units. Substituting for dU from (16) in (17), we get

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV.$$

and dividing by dT we have

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{\partial V}{\partial T}$$

Now $\frac{\delta Q}{dT} = C$, the gram-molecular specific heat. If volume be kept constant,

$$\left(\frac{\delta Q}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v = C_v \quad . \quad . \quad . \quad . \quad . \quad (18)$$

from definition. If pressure be kept constant, $\left(\frac{\delta Q}{dT}\right)_p = C_p$, the specific heat at constant pressure. Hence

$$C_p = \left(\frac{\partial U}{\partial T}\right)_v + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \quad . \quad . \quad . \quad (19)$$

For a perfect gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and $p\left(\frac{\partial V}{\partial T}\right)_p = R$, hence using (18)

* It is thus seen that the quantity dU is a perfect differential of a function U of the variables defining the state of the body; we can therefore write dU in place of δU. In contrast with this the quantities, δQ, δW are not perfect differentials. This is readily seen from the indicator diagrams since the values of δQ and δW depend upon the path of the transformation and not only upon the initial and final states. Hence we have denoted these changes by δQ and δW. Some people use d in place of these δ's but then this d should not be taken in the 'differential' sense. δV is however a perfect differential and we can write $\delta W = pdV$.

we get

$$C_p - C_v = R. \qquad \qquad (20)$$

as has been deduced on p. 46. The relation for solids and liquids is complicated (see sec. 38, Example 1).

It is easy to see that δQ, the heat added, cannot be determined only from the initial and final states of the body, and a knowledge of how the heat has been added is essential. Hence C, the specific heat, has no significance unless the external conditions are prescribed. We have defined C_p and C_v, but there may be other processes, *e.g.*, adiabatic, when $\delta Q = 0$ and $C = 0$.

11. Work done in Certain Processes.— The following expressions for work done in different processes have been already proved:—

(*a*) Work done by a perfect gas in isothermal expansion is (*vide* p. 215) equal to

$$RT \log_e(V_b / V_a).$$

(*b*) Work done by a perfect gas in adiabatic expansion in which the temperature falls from T_1 to T_2 is (*vide* p. 215)

$$= R\frac{(T_1 - T_2)}{\gamma - 1}.$$

(*c*) In the case of a cyclic process the substance returns to its initial state and hence $dU = 0$. Equation (17) then yields $dQ = pdV/J$, *i.e.*, the heat absorbed by the substance is equal to the external work done by it during the cyclic process. Thus in Carnot's cycle the work done during a cycle is $Q_1 - Q_2$.

12. Discontinuous Changes in Energy—Latent Heat— When a body is in the condensed state (solid or liquid) and is subjected to increasing temperature, the state may suddenly change from solid to liquid form (fusion), or from liquid to gaseous form (evaporation), or from one crystalline form to another (allotropic modification). In such discontinuous changes the energy also changes discontinuously (phenomena of latent heat). Let us consider the evaporation of 1 gram of water at 100°C, and 1 atm. pressure. The application of First Law yields

$$L = u_2 - u_1 + p(v_2 - v_1), \qquad \qquad (21)$$

where u_2, v_2 respectively denote the internal energy and volume of 1 gram of vapour, and u_1, v_1 the corresponding quantities for the liquid.

Equation (21) expresses the fact that the heat added is spent in two stages: (1) in converting 1 gram of water to 1 gram of vapour having the same volume, (2) in doing external work, whereby the vapour produced expands under constant pressure to its specific volume.

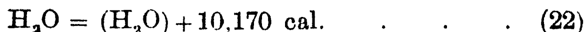
$u_2 - u_1$ is sometimes known as the internal latent heat and $p(v_2 - v_1)$ as the external latent heat. For water at 100°C.,

$v_1 = 1$ c.c., $v_2 = 1674$ c.c. (specific volume of saturated vapour).

Hence $p(v_2 - v_1) = \dfrac{1{\cdot}013 \times 10^6 \times 1673}{4{\cdot}18 \times 10^7}$ cal $= 40{\cdot}5$ cal.

Since $L = 538{\cdot}7$, the Internal Latent Heat $u_2 - u_1 = 498{\cdot}2$ cal.

It is often convenient to denote the different states of aggregation of the same substance according to the following convention. $[H_2O]$, (H_2O), H_2O denote water in the solid, liquid and gaseous states respectively. The quantity taken is always a mol. unless otherwise stated. The symbolical equation



$$H_2O = (H_2O) + 10{,}170 \text{ cal.} \quad . \quad . \quad . \quad (22)$$

expresses the experimentally observed fact that the energy content of a mol of H_2O (gas) at 0°C exceeds the energy-content of a mol of H_2O (liquid) at 0°C. by 10,170 calories, the change taking place at constant volume.

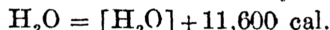
We have further



$$(H_2O) = [H_2O] + 1{,}430 \text{ cal.} \quad . \quad . \quad . \quad (23)$$

i.e., energy of a mol. of liquid H_2O at 0°C. exceeds the energy of a mol of ice at 0°C. by 1,430 cal.

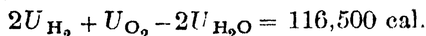
From equations (22) and (23) we have by addition



$$H_2O = [H_2O] + 11{,}600 \text{ cal.}$$

i.e., heat of sublimation of 1 mol. of ice at constant volume is 11,600 calories. This is a consequence of the First Law applied to a physical process and can be easily verified.

13. The First Law applied to Chemical Reactions—Hess's Law of Constant Heat-summation.— The First Law can be extended to Chemical Reactions. Thus when 2 mols of H_2 and 1 mol of O_2 are exploded together in a bomb calorimeter, 2 mols of (H_2O) are formed, and 136,800 calories of heat are evolved. Allowing for the heat evolved in passing from the gaseous to the liquid state, we obtain from the First Law, since $\delta Q = -116{,}500$ and $\delta W = 0$,

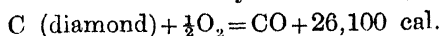


$$2U_{H_2} + U_{O_2} - 2U_{H_2O} = 116{,}500 \text{ cal.}$$

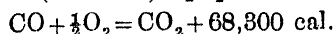
i.e., the energy of 2 mols of H_2 and 1 mol of O_2 exceeds the energy of 2 mols of H_2O by 116,500 calories.

Hess stated in 1840, before the First Law had been discovered, that if a reaction proceeds directly from state 1 to state 2, and again through a series of intermediate states then the heat evolved in the direct change is equal to the algebraic sum of the heats of reaction in the intermediate stages. This is an important law in Thermochemistry and is known as Hess's Law of Constant Heat Summation.

The law is illustrated by the following examples:—

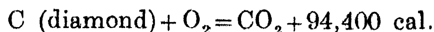


$$C \text{ (diamond)} + \tfrac{1}{2}O_2 = CO + 26{,}100 \text{ cal.}$$



$$CO + \tfrac{1}{2}O_2 = CO_2 + 68{,}300 \text{ cal.}$$

We have by adding



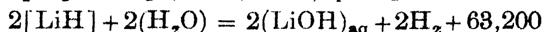
$$C\ (\text{diamond}) + O_2 = CO_2 + 94{,}400\ \text{cal.}$$

This is verified by experiments.

We take another example. Let the symbol $(LiOH)_{aq}$ denote the solution of 1 mol of the substance. Then take the equations:—



$$2[Li] + 2(H_2O) = 2(LiOH)_{aq} + H_2 + 106{,}400$$



$$2[LiH] + 2(H_2O) = 2(LiOH)_{aq} + 2H_2 + 63{,}200$$

The energy evolved is very easily determined from solution experiments. Subtracting the lower equation from the upper one we obtain



$$2[Li] + H_2 = 2[LiH] + 43{,}200\ \text{cal.}$$

i.e., the heat of formation of two mols of [LiH] from [Li] and H_2 is 43,200 cal.

THE SECOND LAW OF THERMODYNAMICS AND ENTROPY

14. Scope of the Second Law.— The Second Law of Thermodynamics deals with a question which is not at all covered by the First Law, *viz.*, the question of the direction in which any physical or chemical process involving energy changes takes place.

A few illustrations will clear the point. Let us consider the thermodynamical process illustrated by the symbolic equation:—



$$2H_2 + O_2 = 2H_2O + U\ \text{calories.}$$

The equation tells us that if 2 mols of H_2 gas combine with one mol of O_2, 2 mols of H_2O-vapour are formed and U calories of heat are evolved, or *vice versa*, when 2 mols of H_2O-vapour are decomposed completely into H_2 and O_2, U calories of heat must be absorbed. This result is obtained as a matter of experience from calorimetric experiments, and we interpret the result according to the First Law of Thermodynamics by saying that in the combination of 2 molecules of hydrogen with 1 molecule of oxygen to form 2 molecules of H_2O, the diminution in energy amounts to JU/N ergs. This result can be further utilised in calculating energy relations in other reactions. But the first law cannot tell us in which direction the reaction will take place. If we have a mixture consisting of H_2, O_2 and H_2O-vapour in arbitrary proportions at some definite temperature and pressure, the first law cannot tell us whether some H_2 and O_2 will combine to form H_2O or some H_2O will dissociate into H_2 and O_2, the system thereby passing to a state of greater stability.

Or we can take a physical example. When two bodies, A and B, exchange heat, the first law tells us that the heat lost by one body is equal to the heat gained by the other. But it does not tell us in which direction this heat will flow. Only experience tells us that heat will pass from the hotter body to the colder one spontaneously,

but in speaking of hotter and colder bodies we are making use of a new physical concept (temperature) which is not at all included within the scope of the first law. For giving us guidance in deciding the question of direction in which a process will take place, we require a new principle and this principle, which arose out of Carnot's speculations about the convertibility of heat to work, is generally known as the *Second Law of Thermodynamics.*

15. Preliminary Statement of the Second Law.— The problem of convertibility of heat to work has been treated in Chap. IX. It is readily observed that the main question there was about the direction of energy transformation. Mechanical energy and heat are only different forms of energy, but while mechanical energy can be completely converted to heat by such processes as friction, it is not possible to convert heat completely to work. Even by using reversible engines which are the most efficient, only a fraction can be converted to work. The conversion is therefore only partial. The question is, why is it so?

An answer to this question has been given already in Chap. IX, *viz.*, if it were possible to design an engine more efficient than a reversible engine, we could continuously convert heat to work, and this will produce perpetual motion of a kind. We may call this *perpetual motion of the second kind.* We are convinced that this is not possible, and we may start from a statement which expresses our conviction just as the first law is based on the conviction that Energy cannot be created, but can only be transformed. We may make the statement in the following form:—

"*It is impossible to construct a Heat Engine which will continuously abstract heat from a single body, and convert the whole of it to work without leaving changes in the working system.*" This statement is equivalent to Clausius or Lord Kelvin's statement of the Second Law.

Lord Kelvin stated the law in this form:—"*It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*"

Clausius stated it in the form:—"*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature, or heat cannot of itself pass from a colder to a warmer body.*"

It must be clearly understood that these statements refer to continuous or cyclical processes. For it is always possible to let heat pass from a colder to a hotter body and at the same time the substance may change to a state different from its initial one. As an example consider an isolated system comprised of a cold compressed gas and a hot rarefied gas communicating with each other through a movable piston. When the piston is released, the hot vapour is compressed and heat is thereby transferred from the cold to the hot gas. The state of the two gases however changes as a result of the process.

To face p. 248



LORD KELVIN (p. 248)

William Thomson, Lord Kelvin of Largs, born on June 26, 1824, in Belfast died on December 17, 1907. His important contributions to Heat are the Second Law, the absolute thermometric scale and the Joule-Kelvin effect. He carried on valuable researches in Electricity.



RUDOLF CLAUSIUS (1822—1888) (p. 248)

Born at Köslin, he studied in Berlin and became Professor of Physics successively at Zürich, Würzburg and Bonn. Simultaneously with Lord Kelvin he announced the Second Law of Thermodynamics. He was one of the founders of the Kinetic Theory of Gases.

16. Absolute Scale of Temperature.— Lord Kelvin showed in 1884 that with the aid of the ideal Carnot engine it was possible to define temperature in terms of energy; and the scale so obtained is independent of the nature of any particular substance. Kelvin started from the result (p. 219) that the efficiency of all reversible engines working between two temperatures is a function of the two temperatures only and is independent of the nature of the working substance. This may be mathematically stated in the form

$$\frac{W}{Q_1} = f(\theta_1, \theta_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where W is the work done by the Carnot engine, Q_1 the heat taken in and θ_1, θ_2 the temperatures* between which the engine works.

Now $W = Q_1 - Q_2$ where Q_2 is the heat rejected. Hence

$$\frac{Q_1 - Q_2}{Q_1} = f(\theta_1, \theta_2),$$

or

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2),$$

where F denotes some other function of θ_1 and θ_2.

It can be easily shown that the ratio Q_1/Q_2 can be expressed in the form $\psi(\theta_1)/\psi(\theta_2)$. For if we have reversible engines working between the pairs of temperatures (θ_1, θ_2), (θ_2, θ_3), (θ_1, θ_3) and the heat absorbed or evolved (as the case may be) at these temperatures be Q_1, Q_2, Q_3, then

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2), \quad \frac{Q_2}{Q_3} = F(\theta_2, \theta_3), \quad \frac{Q_1}{Q_3} = F(\theta_1, \theta_3). \quad . \quad (25)$$

From these by multiplying the first two expressions we get

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3).$$

Hence the function F must satisfy the relation

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3). \quad . \quad . \quad . \quad . \quad (26)$$

This will be so only when $F(\theta_1, \theta_2)$ is of the form $\psi(\theta_1)/\psi(\theta_2)$. Therefore for any reversible engine

$$\frac{Q_1}{Q_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

It will be seen that if $\theta_1 > \theta_2$, $Q_1 > Q_2$ and therefore $\psi(\theta_1) > \psi(\theta_2)$, i.e., $\psi(\theta)$ is a quantity which increases monotonically with θ and may be used to measure temperature. Denote the value of $\psi(\theta)$ by τ.

The relation (27) then becomes

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

* These may be measured on any arbitrary scale.

Equation (28) is used to define a new scale of temperature τ which is called the absolute or the thermodynamic scale. This scale does not depend upon the properties of any particular substance for equation (28) is universally true. The ratio of any two temperatures on this scale is equal to the ratio of the heat taken in and heat rejected by an engine working reversibly between the two temperatures.

The zero of this scale ($\tau=0$) is that temperature at which $Q_2 = 0$ (from 28) and hence $W = Q_1$. Thus all the heat taken by the engine has been converted into work and the efficiency of the engine is unity. τ cannot be less than this, i.e., negative, for if it were so, Q_2 would be negative which implies that the engine would be drawing heat both from the source and the sink. This is impossible from the second law and hence $\tau = 0$ is the lowest temperature conceivable. This is the absolute zero of temperature which need not be the temperature at which all molecular motions cease to exist as one might otherwise infer from elementary kinetic theory.

The zero having been determined, let us fix the size of the degree. In conformity with general usage we suppose that the interval between the freezing and the boiling points of water is divided into 100 equal parts on this scale, *viz.*,

$$\frac{Q_{steam}}{Q_{ice}} = \frac{\tau_{ice} + 100}{\tau_{ice}} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The thermodynamic scale has thus been completely defined and fixed. Let us see how this scale can be actually realised in practice.

For this we must investigate the property of some actual substance. A perfect gas is very suitable for this purpose. In fact we have already shown on p. 216 that for a Carnot engine using a perfect gas as the working substance,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where T_1, T_2 are the temperatures measured on the perfect gas scale. Equation (28) combined with (30) yields

$$\frac{\tau_1}{\tau_2} = \frac{T_1}{T_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

i.e., the ratios of any two temperatures on the thermodynamic scale and the perfect gas scale are equal. Thus the absolute zero of the thermodynamic scale coincides with the zero of the perfect gas thermometer; for if $\tau_2 = 0$, $T_2 = 0$. Further from (29) and (31) since the interval between the ice point and steam point is 100° on both scales, τ_{ice} and T_{ice} are identical, and in general from (31) other temperatures on the two scales are also identical. Thus the thermodynamic scale is given by the perfect gas thermometer. For the methods of reducing the ordinary gas scale to perfect gas scale see p. 9.

ENTROPY

17. Definition of Entropy.— The formulation of the Second Law, as on p. 248, is not of much use for finding out the direction of change in a chemical or physical process. We want a more general and mathematical formulation which was supplied by Clausius.

Clausius shifted the interest from the problem of convertibility of heat to work, to that of change of thermal state of the working substance, for it is only the working substance which undergoes a thermodynamical change in the process. He observed that when the heat Q is added to it reversibly at temperature T, and Q' taken away from it reversibly at temperature T' we have

$$\frac{Q}{T} - \frac{Q'}{T'} = 0. \qquad . \quad . \quad . \quad . \quad . \quad (32)$$

This property was utilised in defining an additional thermodynamical function (Entropy) for the gas which proved to be of great importance in the further development of thermodynamics. In the following deduction, we have followed Ewing's treatment.*

Let us take a gas in a definite state A (Fig. 1), and compare this state with another state B, which is obtained by the addition of heat energy. It is easy to see that the amount of heat added from outside may be anything, owing to the variety of ways in which heat can be added. This can be visualised by drawing curves between A and B. There may be an infinite number of curves passing between A and B, corresponding to the infinite number of ways in which heat can be added and for all these the amount δQ of heat added will be different. It will be shown, however, that the integral

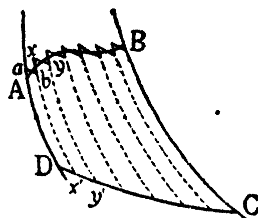


Fig. 1.—The entropy function.

$$\int_A^B \frac{\delta Q}{T}$$

measured along any reversible process does not depend on the path, but only on the coördinates of A and B.

Let us draw two adiabatics through A and B and draw an isothermal DC at temperature t cutting these adiabatics in D and C respectively. Let us now divide the area ABCD into a number of elementary Carnot cycles $xyy'x'$ as in Fig. 1 (xy, $x'y'$, isothermals, and xx', yy' adiabatics).

Let δQ be the amount of heat absorbed at temperature T while

* See Glazebrook, *A Dictionary of Applied Physics*, Vol. I, p. 271.

the point shifts from x to y and δq be the amount given up while it shifts from y' to x'. Then we have

$$\frac{\delta Q}{T} = \frac{\delta q}{t}.$$

Adding up for all the Carnot cycles between A and B, we have

$$\Sigma\frac{\delta Q}{T} = \Sigma\frac{\delta q}{t} = \frac{1}{t}\Sigma\delta q. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

This is the value of $\int\frac{\delta Q}{T}$ along the zigzag path A$abxy$.........B, for the value of the integral along the adiabatics Aa, bx,......... is 0.

In the limiting case when the Carnot cycles are infinitely small the zigzag path Aabx......B coincides with AB. Hence

$$\int_{A}^{B}\frac{\delta Q}{T} = \Sigma\frac{\delta Q}{T} = \frac{1}{t}\Sigma\delta q. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

The value of the integral $\int_{A}^{B}\frac{\delta Q}{T}$ is now seen to be equal to $\Sigma\delta q/t$ and hence it is independent of the path between A and B.

Instead of taking the particular isothermal DC we may draw any other isothermal cutting AD and BC, the value of the integral cannot be thereby changed, for if we construct a number of Carnot cycles between the first and the second isothermals we have

$$\frac{1}{t}\Sigma\delta q = \frac{1}{t'}\Sigma\delta q'.$$

The points A and B may be taken anywhere on the adiabatics AD and BC respectively, the value of the integral will remain the same, for $\int\frac{\delta Q}{T}$ along an adiabatic is zero since $\delta Q = 0$. Hence it follows that if we pass from one adiabatic to another the expression $\int_{1}^{2}\frac{\delta Q}{T}$ denotes a quantity which increases by a fixed amount independent of the manner of transformation. If we start from some zero state and denote the value of the integral $\int_{0}^{A}\frac{\delta Q}{T}$ by s_A it follows that s_A is a function of the coordinates of A alone. Clausius called it the *entropy* of the substance. Now since we are not familiar with the zero state of the body when it will be deprived of all its heat, we cannot find in this way the absolute value of the entropy in any state. We are however generally concerned with changes in entropy and hence we can measure from any arbitrary zero as is done in the case of energy. To measure the entropy in any state we have to take the substance along any reversible process to its zero state and find the value of $\Sigma\delta q/t$ along this process. The entropy, though conveniently measur-

ed with respect to a reversible process, has nothing to do with it and exists quite independently of it.

The above treatment is perfectly general and will hold whatever substance is taken as the working substance. Now if the work is done by expanding against an external pressure we have from the first law for any process reversible or irreversible, $\delta Q = du + pdv$, where p stands for the external pressure at every stage of the process. But for finding entropy we have to substitute the value of δQ along a reversible process. Now the process is reversible only when the external pressure p is always equal to the intrinsic pressure of the substance, i.e., when the expansion is balanced. Hence we get*

$$s = \int^T \frac{du + pdv}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where p denotes the pressure of the substance itself.

It is easily seen that entropy is proportional to the mass of the substance taken, for if we take M grams of the substance $dU = Mdu$, $dV = Mdv$ and hence $S = Ms$.

Exercise.—Find the increase of entropy when 10 grams of ice at 0°C. melt and produce water at the same temperature, given that the latent heat of fusion of ice=80 calories/gm.

Since the process is reversible and isothermal we have

$$\triangle S = \frac{10 \times 80}{273} = 2{\cdot}93 \text{ cal./degree C.}$$

18. Entropy of a System.— In the last section it was shown that if the entropy per unit mass of a substance is s the entropy of m grams of the substance is ms. It can be shown in a similar way that if we have a system of bodies in *thermodynamical equilibrium* with different thermodynamical variables and having masses m_1, m_2. . and specific entropies s_1, s_2. . ., the entropy of the whole system is

$$S = m_1 s_1 + m_2 s_2 + \ldots \quad , \quad . \quad . \quad . \quad . \quad (36)$$

19. Entropy remains Constant in Reversible Processes.— The sum of the entropies of all systems taking part in a *reversible* process remains constant. Considering the Carnot cycle we notice that the working substance has the same entropy at the end of the cycle as at the beginning since it returns to the same state. The loss in entropy of the source is Q_1/T_1, the gain by the condenser is Q_2/T_2, and hence the net gain in the entropy of the system is

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Thus the entropy of the whole system remains constant.

* A more general definition is the following :—If from any cause whatever, the unavailable energy of a system with reference to another system at T_0 undergoes an increase $\triangle E$, then $\triangle E/T_0$ measures the increase of entropy of the system.

In the *isothermal expansion* of the working substance in the first part of the Carnot cycle the increase in entropy of the working substance is Q_2/T_2, the loss by the source is Q_1/T_1 and hence the total entropy remains constant. This holds for any reversible transformation.

Working out as on p. 215 we see that the increase in entropy of a gram-molecule of perfect gas in isothermal expansion from volume V_1 to V_2 at temperature T is

$$\triangle S = \int_{V_1}^{V_2} \frac{dU+pdV}{T} = \frac{1}{T}\int_{V_1}^{V_2} pdV = R \; ln^* \; \frac{V_2}{V_1} \qquad (38)$$

The change in entropy during a *reversible adiabatic compression or expansion* is zero. For in such a process the external work done is $\int pdV$ and change in entropy is $\triangle S = \int \frac{dU+pdV}{T}$, but by the condition of the process from the first law $dU+pdV = 0$, hence the entropy remains constant in an adiabatic process. Adiabatic curves are therefore sometimes known as "*Isentropics*."

20. Entropy Increases in Irreversible Processes.— The entropy of a system increases in all irreversible processes. As examples of such processes we may mention the conduction or radiation of heat, the rushing of a gas into a vacuum, the inter-diffusion of two gases, the development of heat by friction, flow of electricity in conductors, etc. We shall prove the theorem here for a few cases.

(i) Increase of Entropy during Conduction or Radiation of Heat.— Suppose a small quantity of heat Q is conducted away from a body A at temperature T_1 to another body B at temperature T_2 $(T_1 > T_2)$, and let δQ be so small that the temperatures T_1 and T_2 of the bodies are not appreciably altered in the process, then A loses entropy equal to $\frac{\delta Q}{T_1}$ while B gains entropy by an amount $\frac{\delta Q}{T_2}$. Thus the total gain in entropy of the two bodies is

$$\triangle S = \delta Q \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (39)$$

which is positive since $T_1 > T_2$. Hence the entropy of the system as a whole increases during thermal conduction. Similarly in the case of radiation, if a quantity of heat δQ is radiated from the body A to the body B, the gain in entropy is given by the same expression. Thus increase of entropy is always produced by the equalisation of temperature.

(ii) Gas rushing into a vacuum.—Consider a perfect gas in a vessel rushing into an evacuated vessel and let the whole system be isolated. Since the gas is perfect the temperature does not change

* *ln* denotes natural logarithm.

in the process. The gain in entropy may be obtained by finding the value of $\int \frac{\delta Q}{T}$ along any reversible path connecting the initial and final states. The reversible process most convenient for this purpose is an isothermal expansion of the gas against a pressure which is always just less than the pressure of the gas.

$$\therefore \quad \int \frac{\delta Q}{T} = \frac{1}{T}\int \delta Q = \frac{1}{T}\int_{V_1}^{V_2} (dU + pdV).$$

For a perfect gas dU at constant temperature is zero. Hence the gain in entropy

$$\triangle S = \frac{1}{T}\int pdV = R \ln \frac{V_2}{V_1}, \quad . \quad . \quad (40)$$

where V_1, V_2 denote the initial and final volumes of the gas. Hence the entropy of the system increases in this irreversible process.

21. The Entropy of a Perfect Gas.— Let us take m grams of a perfect gas having the temperature T and occupying the volume v. The entropy ms is given by the relation

$$ms = \int_0^T \frac{du + pdv}{T}.$$

Since $du = mc_v dT$, $p = mRT/Mv$, we have

$$ms = m(c_v \ln T + \frac{R}{M} \ln v) + \text{const.} \quad . \quad . \quad . \quad (41)$$

We can also express ms in terms of pressure. From the relation

$$c_p = c_v + \frac{R}{M}$$

we get $$ms = m(c_p \ln T - \frac{R}{M} \ln p) + \text{const.} \quad . \quad . \quad . \quad (42)$$

Exercise.—Calculate the increase in entropy of two grams of oxygen when its temperature is raised from 0° to 100°C and its volume is also doubled.

$$\triangle S = 2 \times 2{\cdot}3026 \left[\frac{5{\cdot}035}{32} \log \frac{373}{273} + \frac{1{\cdot}986}{32} \log 2\right] = 0{\cdot}184 \frac{\text{cal.}}{\text{deg}}$$

22. General Statement of Second Law of Thermodynamics.— We have shown above for a few irreversible processes that increase of entropy takes place during such a process. This result is however very general and holds for any process occurring of itself. We shall not attempt to prove here this general statement, but only enunciate it in the following words:—*Every physical or chemical process in nature takes place in such a way that the sum of entropies of all bodies taking part in the process increases. In the limiting case of a reversible process the sum of entropies remains constant.* This is the most general statement of the Second Law of Thermodynamics and is iden-

tical with the *Principle of Increase of Entropy*, viz., the entropy of a system of bodies tends to increase in all processes occurring in nature, if we include in the system all bodies affected by the change.

Clausius summed up the First Law by saying that *the energy of the world remains constant* and the Second Law by saying that *the entropy of the world tends to a maximum*. Though the terms 'energy of the world' and 'entropy of the world' are rather vague, still, if properly interpreted, these two statements sum up the two laws remarkably well.

23. Supposed Violation of the Second Law.— Maxwell invented an ingenious contrivance which violates the Second Law as enunciated above. Following Boltzmann's idea, he imagined an extraordinary being who could discriminate between the individual molecules. Suppose such a creature, usually known as Maxwell's demon, stands at the gate in a partition separating two volumes of the same gas at the same temperature and pressure and, by opening and shutting the gate at the proper moment, allows only the faster moving molecules to enter one enclosure and the slower molecules to enter the other enclosure. The result will be that the gas in one enclosure will be at a higher temperature than in the other and the entropy of the whole system thereby decreases, though no work has been done. This apparently violates the Second Law.

We observe, however, that to Maxwell's demon the gas does not appear as a homogeneous mass but as a system composed of discrete molecules. The law of entropy does not hold for individual molecules, but is a *statistical law* and has no meaning unless we deal with matter in bulk.

24. Entropy and Unavailable Energy.— Consider a source at temperature T_1 and suppose it yields a quantity of heat Q to a working substance. If the lowest available temperature for the condenser of the Carnot cycle is T_0 the amount of heat rejected by the Carnot engine working between T_1 and T_0 is QT_0/T_1. The remainder, *i.e.* $Q - Q\dfrac{T_0}{T_1}$ has been converted into work. Thus the available energy is $Q\left(1 - \dfrac{T_0}{T_1}\right)$. Now suppose a quantity of heat δQ passes by conduction from a body at temperature T_2 to another at temperature T_3. The unavailable energy initially was $(T_0/T_2)\delta Q$ and finally it was $(T_0/T_3)\delta Q$. Hence the gain in unavailable energy is $\delta Q\left(\dfrac{1}{T_3} - \dfrac{1}{T_2}\right)T_0$, T_0 being the lowest available temperature. The increase in entropy of the system is, as we have already proved, equal to $\delta Q\left(\dfrac{1}{T_3} - \dfrac{1}{T_2}\right)$. Hence the increase of unavailable energy is equal to the increase of entropy multiplied by the lowest temperature available. Thus entropy is a

measure of the unavailability of energy, and the law of increase of entropy implies that the available energy in the world tends to zero, *i.e.*, energy tends to pass from a more available form to a less available form. This is the law of degradation or dissipation of energy mentioned on p. 243 and is thus seen to be equivalent to the Second Law. It follows as a corollary that all transformations, physical or chemical, involving changes of energy will cease when all the energy of the world is run down to its lowest form.

25. Physical Concept of Entropy.— The entropy of a substance is a real physical quantity which remains constant when the substance undergoes a reversible adiabatic compression or expansion. It is a definite single-valued function of the thermodynamical coordinates defining the state of the body, viz., the temperature, pressure, volume or internal energy as explained on p. 237. It is difficult to form a tangible conception of entropy because there is nothing physical to represent it; it cannot be felt like temperature or pressure. It is a statistical property of the system and is intimately connected with the *probability of that state.* Growth of entropy implies a transition from a more to a less available energy, from a less probable to a more probable state, from an ordered to a less ordered state of affairs. The idea of entropy is necessitated by the existence of irreversible processes. It is measured in calories per degree or ergs per degree.

26. Entropy-Temperature Diagrams.— We have represented the Carnot cycle and other cycles in Chap. IX by means of the usual indicator diagram in which the volume denotes the abscissa and the pressure denotes the ordinate. Another way to represent the cycle, which is often found very useful, is by plotting the temperature of the working substance as ordinate and the entropy as abscissa. Its importance is readily perceived for during any reversible expansion the increase dS in entropy is given by

$$dS = \frac{dQ}{T}.$$

$$\therefore \int TdS = \int dQ,$$

where the integration is performed between the limits of the expansion. Thus the area of the curve on the entropy-temperature diagram represents the amount of heat taken up by the substance.

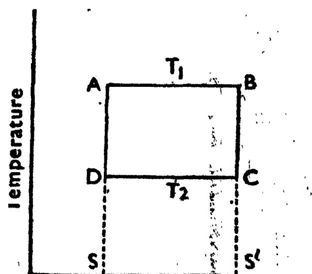


Fig. 2.—Entropy-temperature diagram of Carnot cycle.

The Carnot cycle can now be easily represented on the entropy-temperature diagram by Fig. 2. AB represents the isothermal expansion at T_1, BC the reversible adiabatic expansion, CD the isothermal compression at T_2, the temperature of the sink, and DA the final adiabatic compression. It is evident that lines AB and CD will be parallel to the entropy-axis and BC, AD will be parallel to the tem-

perature-axis. The amount of heat taken in is represented by the area ABba, heat rejected by the area DCba, the difference ABCD being converted into work. These areas are respectively $T_1(S'-S)$, $T_2(S'-S)$, (T_1-T_2) $(S'-S)$ and the efficiency is $1-T_2/T_1$.

27. Entropy of Steam.— For enabling the student to have a proper grasp of the conception of entropy we shall calculate the entropy of steam. Let us start with 1 gram of water at 0°C. and go on adding heat to it. The increase in entropy when we add a small amount of heat δQ at $T°$ is $\frac{\delta Q}{T}$. But $\delta Q = \sigma dT$ where σ is the specific heat of water at constant pressure. Hence the entropy of water at $T°$ is

$$s = s_0 + \int_{T_0}^{T} \frac{\sigma dT}{T} = s_0 + \sigma \log_e \frac{T}{T_0},$$

if σ is assumed to be constant. s_0 denotes the entropy of water at (0°C) (T_0°K.) and it is customary to put it equal to zero. Hence for water

$$s = \sigma \log_e \frac{T}{273},$$

where σ can be put equal to unity. This is represented by the logarithmic curve OA in Fig. 3.

If the liquid is further heated it boils at the temperature T_1 absorbing its latent heat L. Since the temperature remains constant in this process the increase in entropy per gram is L/T_1. This is represented by AB in the figure. Hence the entropy of 1 gram of dry saturated steam is

$$s = \sigma \log_e \frac{T_1}{273} + \frac{L}{T_1}.$$

If the steam is wet, q being its dryness, *i.e.*, q is the proportion of dry steam in the mixture expressed as a fraction of the whole, the entropy of wet steam is

$$= \sigma \log_e \frac{T_1}{273} + \frac{qL}{T_1}.$$

If the steam is superheated to $T_2°$ the entropy is further increased by the amount $\int_{T_1}^{T_2} c_p \frac{dT}{T}$ where c_p denotes the specific heat of steam during superheating. This is represented by BC in the figure. Hence the entropy of superheated steam at $T_2°$ is

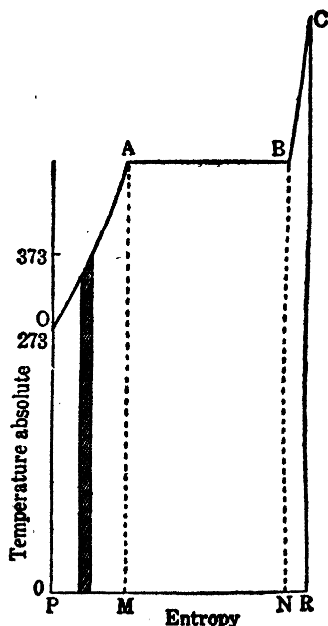


Fig. 3.—Entropy-temperature diagram of steam.

$$s = \sigma \log_e \frac{T_1}{273} + \frac{L}{T_1} + \int_{T_1}^{T_2} c_p \frac{dT}{T}.$$

As c_p varies with temperature, its average value over small intervals is taken. In this way the entropy of steam in any state can be calculated.

Exercise.—Find the entropy of saturated steam at a pressure of 74 lb. per sq. in.

From the table the boiling point at this pressure is 152·6°C. and the latent heat at this temperature is 503·6 cal./gm. The entropy of 1 gm. of water at 152·6°C or 425·6°K is $1 \times \log_e 425{\cdot}6/273 = 0{\cdot}44$ cal./degree. The increase in entropy due to the evaporation at 425·6°K is $503{\cdot}6/425{\cdot}6 = 1{\cdot}18$ cal./degree. Therefore the entropy of steam at 425·6°K is given by $\cdot 44 + 1{\cdot}18 = 1{\cdot}62$ cal./degree. This may be verified by looking at the steam tables. For more accurate calculation the variation of the specific heat of water with temperature should be taken into account.

APPLICATIONS OF THE TWO LAWS OF THERMODYNAMICS

28. General Considerations.—For making frequent and effective use of the Second Law, it should be expressed in a convenient form. For this purpose a mathematical formulation is more desirable and was supplied by Clausius (p. 252). *viz.*,

$$\delta Q = T ds^*, \quad . \quad . \quad . \quad . \quad . \quad (43)$$

where δQ is the heat absorbed during a reversible process connecting the two states. From the first law

$$\delta Q = du + p dv, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where p denotes the intrinsic pressure of the substance and is given by its equation of state. Combining these two equations we get

$$du + p dv = T ds. \quad . \quad . \quad . \quad . \quad (44)$$

Let us further investigate the nature of the variations du, dv and ds. As already stated in Chap. IV and also on p. 237, the state of every substance is fixed if we know any two of the variables p, v, T, u....... For example, the internal energy $u = f(v, T)$ is uniquely defined if v and T are given. Thus if we represent the internal energy u of the substance on the coordinate system v, T, the value of u for every point is fixed and does not depend upon the path along which we bring the substance to that point (state); in other words, the total change du has the same value whether we first make the change dv in v and then the change dT in T or in the reverse order.

* The results deduced from this equation in the following pages and their confirmation by experiments may be taken as direct verification of this equation and therefore of the Second Law.

Mathematically, this means that du is a perfect differential and as explained on p. 239 we must have

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

where x and y are the two variables defining the state of the system.

The entropy function was shown on p. 252 to be such that its value does not depend upon the path of transformation, *i.e.*, s is also a single-valued function of the coordinates. Similar is the case with the volume and the internal energy.

As a contrast and for clearer understanding, it may be mentioned that pdv and $\delta Q = du + pdv$ are not perfect differentials for their values depend upon the path of transformation. This may be easily seen as $\int vdv$ represents the area of the indicator diagram and has different values for different paths. But though $du + pdv$ is not integrable we have proved by physical arguments, that $(du + pdv)/T$ is integrable; in other words, $1/T$ is the integrating factor to the energy equation.

We now proceed to make use of the above ideas for the further development of equation (44).

29. The Thermodynamical Relationships (Maxwell).—Equation (44) may be written as

$$du = Tds - pdv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Now if x and y are any two independent variables we have, since u, s and v are expressible in terms of x and y,

$$ds = \frac{\partial s}{\partial x} dx + \frac{\partial s}{\partial y} dy,$$

$$dv = \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy,$$

and

$$du = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy.$$

Substituting the values of ds, dv, du in (46) and equating the coefficients of dx, dy, we get

$$\frac{\partial u}{\partial x} = T\frac{\partial s}{\partial x} - p\frac{\partial v}{\partial x},$$

$$\frac{\partial u}{\partial y} = T\frac{\partial s}{\partial y} - p\frac{\partial v}{\partial y}.$$

Now, since du is a perfect differential, we should have

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x}.$$

or

$$\frac{\partial}{\partial x}\left(T\frac{\partial s}{\partial y} - p\frac{\partial v}{\partial y}\right) = \frac{\partial}{\partial y}\left(T\frac{\partial s}{\partial x} - p\frac{\partial v}{\partial x}\right).$$

Expanding out and remembering that $\frac{\partial^2 v}{\partial x \partial y} = \frac{\partial^2 v}{\partial y \partial x}$ and $\frac{\partial^2 s}{\partial x \partial y} = \frac{\partial^2 s}{\partial y \partial x}$, we get

$$\frac{\partial T}{\partial x} \cdot \frac{\partial s}{\partial y} - \frac{\partial T}{\partial y} \cdot \frac{\partial s}{\partial x} = \frac{\partial p}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial p}{\partial y} \frac{\partial v}{\partial x}, \quad . \quad . \quad . \quad . \quad (47)$$

which when geometrically interpreted means that the corresponding elements of area whether represented on T, s or p, v coordinates are equal. This relation will hold for a simple homogeneous substance.

For convenience of remembering we may write (47) as

$$\frac{\partial (T, s)}{\partial (x, y)} = \frac{\partial (p, v)}{\partial (x, y)},$$

where $\frac{\partial (T, s)}{\partial (x, y)}$ stands for the determinant

$$\begin{vmatrix} \frac{\partial T}{\partial x} & \frac{\partial T}{\partial y} \\ \frac{\partial s}{\partial x} & \frac{\partial s}{\partial y} \end{vmatrix}.$$

Any two of the four quantities T, s, p, v can be chosen as x, y. This can be done in six different ways and correspondingly, we have six thermodynamical relationships, though all of them are not independent.

30. First Relation.—Let us take the temperature and the volume as independent variables, and put $x = T$, $y = v$ in (47). Then

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial v}{\partial y} = 1,$$

and

$$\frac{\partial T}{\partial y} = \frac{\partial T}{\partial v} = 0; \quad \frac{\partial v}{\partial x} = 0,$$

since T and v are independent. Hence we have

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (48)$$

which implies that the increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temperature when the volume is kept constant. We can apply equation (48) to the equilibrium between the two states of the same substance. Multiplying both sides by T

$$\left(\frac{\delta Q}{\delta v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (49)$$

which means that latent heat of isothermal expansion is equal to the product of the absolute temperature and the rate of increase of pressure with temperature at constant volume. Thus, if a body

changes its state at T° and absorbs the latent heat L, and the specific volumes in the first and the second states are v_1, v_2, equation (49) yields

$$\frac{L}{v_2-v_1} = T\frac{\partial p}{\partial T},$$

or

$$\frac{\partial p}{\partial T} = \frac{L}{T(v_2-v_1)}. \qquad (50)$$

This is Clapeyron's equation and is one of the most useful formulæ in thermodynamics. A more rigorous proof of this will be given in sec. 39.

Let us first employ (50) to find the change in the freezing point of a substance by pressure. In the case of water at 0°C.,

$L = 79{\cdot}6\times4{\cdot}18\times10^7$ ergs per gm.

$T = 273.$

$v_2 = 1{\cdot}000$ c.c. (specific volume of water at 0°C.).

$v_1 = 1{\cdot}091$ c.c. (,, ,, ,, ice at 0°C)

$$\therefore\frac{\partial p}{\partial T} = \frac{79{\cdot}6\times4{\cdot}18\times10^7}{273\times(1-1{\cdot}091)}.$$

Now if $\delta p = 1$ atmosphere $= 1{\cdot}013\times10^6$ dyne/cm²,

$$\delta T = -0{\cdot}0075^\circ.$$

This shows that the melting point of ice is lowered by increase of pressure, the lowering per atmosphere being 0·0075°. The pressure necessary to lower the melting point by 1°C. is 1/·0075 = 133 atm./cm². This accounts for the phenomenon of Regelation of ice and the experiment of Tyndall (p. 110).

These results were quantitatively verified by Kelvin. His experimental results are given in Table 1.

Table 1.—Depression of freezing point with increase of pressure.

Increase of pressure.	Depression of freezing point in °C.	
	observed.	calculated.
8·1 atm.	0·0580	0·0607
16·8 ,,	0·1289	0·1260

For substances which contract on solidification the melting point will be increased by pressure. Thus for acetic acid whose melting point is 15·5°C. de Visser found experimentally that an increase of pressure by 1 atmosphere increases the melting point by 0·02432°C., while equation (50) gave 0·02421°C. This verifies relation (50).

Equation (50) will also hold in the case of fusion of metals. With its help the change in melting point of any substance with pressure can be easily calculated. The values so calculated, together with the experimentally observed values, for a few metals are given in Table 2.* The agreement is fairly satisfactory.

Table 2.—Change in melting point with pressure.

Metal.	Melting point in °C.	Latent heat in cal./gm.	$v_l - v_s$ in c.c. per gm.	δT per 1000 atm. (calc.)	δT per 1000 atm. (obs.)
Sn ...	231·0	14·25	0·003894	+3·34	+3·28
Cd ...	320·4	13·7	0·00564	+5·91	+6·29
Pb ...	326·7	5·37	0·003076	+8·32	+8·03
Bi ...	270·7	12·6	−0·00342	−3·56	−3·55

Equation (50) may also be employed to calculate the latent heat. For the vaporization of water at 100°C. we have the following data:—

$$T = 373°,\ v_1 = 1 \text{ c.c.},\ v_2 = 1674 \text{ c.c. per gram.}$$

$$\frac{dp}{dT} = 27{\cdot}12 \text{ mm. of mercury},$$

$$\therefore\quad L = \frac{373 \times (1674 - 1) \times 27{\cdot}12 \times 1{\cdot}013 \times 10^6}{760 \times 4{\cdot}185 \times 10^7} = 539 \text{ cal./gm.}$$

The accurate experiments of Henning give $L = 538{\cdot}7$ cal. per gm. at 100°C. which is very close to the calculated value. We can also calculate the latent heat of evaporation of water at various temperatures from (50) if we know the values of v_2 and $\frac{\partial p}{\partial T}$ at these temperatures. The values of L so calculated are given in Table 3, together with the observed values. The agreement is seen to be very close.

Table 3.—Latent heat of steam at different temperatures.

t°C.	$\frac{dp}{dT}$ in mm. of Hg.	v_2 in c.c.	L (calc.)	L (obs.) Henning
100	27·12	1674	539·5	538·7
110	36·10	1211	533·4	532·1
120	47·16	892·6	526·6	525·3
130	60·60	669·0	520·1	518·2
140	76·67	509·1	512·9	510·9
150	95·66	393·1	505·7	503·8
160	117·7	307·3	497·5	496·6
170	143·4	243·0	489·8	489·4
180	172·7	194·3	481·8	482·2

* Taken from Jellinek, *Lehrbuch der Physikalischen Chemie*, Vol. 2, p. 517 (1930 edition).

31. Application to a liquid film.— Equation (48) may also be applied to the case of a liquid film. If such a film is stretched, its volume remaining constant, the energy, equation for this case is

$$(\delta Q)_v = du - 2\sigma dA,$$

for the work done by the film is $-2\sigma dA$, where σ is the surface tension and dA the increase in area of the film. The usual term pdv on the right has disappeared since the total volume remains constant. Hence corresponding to p and dv we have in this case -2σ and dA respectively. Therefore equation (49) yields

$$\left(\frac{\delta Q}{\delta A}\right)_{T,v} = -2T\left(\frac{\partial \sigma}{\partial T}\right)_{v,A}$$

and for a finite change

$$\delta Q = -2T\left(\frac{\partial \sigma}{\partial T}\right)_v dA. \quad . \quad . \quad . \quad (51)$$

For a liquid the surface tension decreases with temperature, therefore $\frac{\partial \sigma}{\partial T}$ is negative and δQ is positive. Hence an amount of heat must be supplied to the film when it is stretched in order that its temperature may remain constant. In an adiabatic stretching the temperature will fall by an amount

$$\delta T = \frac{2T}{C_A}\left(\frac{\partial \sigma}{\partial T}\right)_v dA, \quad . \quad . \quad . \quad . \quad (52)$$

where C_A is the heat capacity of the film.

32. Second Relation.— Another important application of the thermodynamic formulæ consists in their application to some adiabatic changes such as the sudden compression of a liquid or sudden stretching of a rod. For this case let us put $x = T$, $y = p$. Equation (47) then reduces to

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad . \quad . \quad . \quad . \quad (53)$$

which means that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temperature during an isobaric process.

Multiplying both sides by T we have

$$\left(\frac{\delta Q}{\delta p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p = -Tv\alpha, \quad . \quad . \quad (54)$$

where α is the coefficient of volume expansion at constant pressure.

From this relation it follows that if α is positive, *i.e.*, the substance expands on heating, $\left(\frac{\delta Q}{\delta p}\right)$ is negative, and hence in this case an amount of heat must be taken away from the substance when the

pressure is increased, in order that the temperature may remain constant. That is, heat is generated when a substance which expands on heating is compressed. For substances which contract on heating, a cooling should take place.

These conclusions were verified experimentally by Joule who worked with fish-oil and water. The liquid was contained in a vessel closed at the top by a piston and pressure was suddenly increased by placing weights upon the piston. The change in temperature was measured by a thermopile. From (54) we can deduce the increase in temperature $\triangle T$ produced by a sudden increase of pressure $\triangle p$. We have*

$$\triangle T = \frac{Tv\alpha}{c_p} \triangle p, \qquad (55)$$

where c_p is the specific heat of the substance and v its specific volume. We have assumed that $v\alpha/c_p$ is independent of pressure, and then integrated for a finite change $\triangle p$ in p. Joule's results with water are very interesting and are given in Table 4.

Table 4.—Increase in temperature of water by sudden increase of pressure.

$\triangle p$ in kg. per cm^2	Initial temp. in °C.	$\triangle T$ (obs.)	$\triangle T$ (calc.)
26·19	1·20	−0·0083	−0·0071
26·19	5·00	+0·0044	+0·0027
26·19	11·69	0·0205	0·0197
26·19	18·38	0·0314	0·0340
26·19	30·00	0·0541	0·0563
26·17	31·17	0·0394	0·0353
26·17	40·40	0·0450	0·0476

The agreement between the observed and the calculated values is seen to be very close. This proves the essential correctness of the theory ; in fact these results formed one of the earliest experimental verifications of the second law. Thus the thermodynamic theory explains the remarkable fact that water below 4°C. cools by adiabatic compression inspite of the fact that the internal energy is increased.

Another series of experiments consists in the adiabatic stretching of wires. The best results were obtained by Haga. The change in temperature of the stretched wire was measured by means of a thermopile formed by the wire itself and another thin wire wound round it. It will be seen that tension means a negative pressure and hence wires of substances which expand on heating should show a cooling when stretched adiabatically. In this case the work done

* We may directly deduce this result from equation (58).

is not pdv but $-Fdl$ hence $\frac{\partial v}{\partial T}$ must be replaced by $\frac{\partial l}{\partial T}$ where l is the length of the wire. Hence in place of (55) we get

$$\triangle T = -\frac{T}{C}\left(\frac{\partial l}{\partial T}\right)_p \triangle F = -\frac{T\beta}{wc_p}\triangle F, \quad . \quad . \quad (56)$$

where β is the coefficient of linear expansion, w the mass per unit length of the wire, c_p its specific heat in mechanical units and C the heat capacity of the wire.

For a German silver wire of diameter 0·105 cm. at room temperature, Haga found the mean value $\triangle T = -0{\cdot}1063$ for a tension of 13·05 kg. and $\triangle T = -0{\cdot}1725$ for 21·13 kg. tension, giving a mean value of 0·00813 per kg. If we substitute the values of w, c_p, β in equation (56) and use the value $J = 4{\cdot}18 \times 10^7$ ergs per cal., we get $\triangle T = -0{\cdot}00810$ in close agreement with the experimental value.

India-rubber when moderately stretched has a negative expansion coefficient. This should show a heating effect when further stretched adiabatically, which is found to be true experimentally and may even be felt by the lips.

33. Other Relations.—Besides the above two, there are other less important relations. Thus putting $x = s$, $y = v$ in (47) we get

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad . \quad . \quad . \quad . \quad (57)$$

This is the third relation. Again putting $x = s$, $y = p$ we get

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \quad . \quad . \quad . \quad . \quad (58)$$

This is the fourth relation. The interpretation of these results is left to the reader.

The above relations are known as Maxwell's four thermodynamic relations. Besides these, there are two more relations which may be obtained by taking p, v, or T, s, as the pair of independent variables. They are

$$\left(\frac{\partial T}{\partial p}\right)_v\left(\frac{\partial s}{\partial v}\right)_p - \left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial s}{\partial p}\right)_v = 1. \quad . \quad . \quad (59)$$

$$\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial v}{\partial s}\right)_T - \left(\frac{\partial p}{\partial s}\right)_T\left(\frac{\partial v}{\partial T}\right)_s = 1. \quad . \quad . \quad (60)$$

These are called the fifth and sixth relations and are much less used.

34. Variation of Intrinsic Energy with Volume.—From the relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$, we find by substituting $\frac{du + pdv}{T}$ for ds

that

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \quad . \quad . \quad . \quad (61)$$

This equation enables us to calculate the variation of intrinsic energy with volume.

For perfect gases* $p = \frac{RT}{V}$, hence $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (Joule's law p. 47).

For gases obeying the van der Waals' law $p = \frac{RT}{(V-b)} - \frac{a}{V^2}$ it can be easily seen by substituting in (61) that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}. \quad . \quad . \quad . \quad . \quad (62)$$

For general systems, we can transform (61) to a form which allows us to calculate $\frac{\partial u}{\partial v}$ from experimental results. This follows from equation (18) of page 240 where it is shown that

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p \quad . \quad . \quad . \quad (63)$$

Hence $$\left(\frac{\partial u}{\partial v}\right)_T = -T\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p - p$$

$$= TE\alpha - p, \quad . \quad . \quad . \quad . \quad . \quad (64)$$

where E = bulk modulus of elasticity, α = coefficient of volume expansion.

We shall compare the ratio $\frac{\partial u}{\partial v} : p$ for a typical liquid, *viz.*, mercury. For mercury at 0° C and atmospheric pressure we have as on p. 240.

$$\left(\frac{\partial p}{\partial T}\right)_v = 46{\cdot}5 \text{ atm. cm}^{-2}\ {}^\circ\text{C}^{-1}$$

Hence $$\frac{1}{p}\left(\frac{\partial u}{\partial v}\right)_T = 46{\cdot}5 \times 273{\cdot}2 - 1 = 12700.$$

Now $\frac{\partial u}{\partial v}$ is sometimes known as the internal pressure the idea being that the visible pressure is equal to the force per sq. cm. with which the particles bombard a layer inside the liquid minus the internal pressure, *i.e.* force/cm² with which they are drawn inwards due to forces of cohesion. The above comparison shows that for

* U, V refer to a gram-molecule, hence $\frac{\partial U}{\partial V} = \frac{\partial u}{\partial v}$ in general. In the text both forms have been used.

ordinary liquids, this force is very great but when we increase the temperature, the ratio diminishes till it vanishes when the perfect gas stage is reached.

35. The Joule-Thomson Effect.—In Chapter VI, we proved that in the Joule-Thomson expansion $u+pv$ remains constant while the pressure changes on the two sides of the throttle valve. Let us calculate the change in temperature due to an infinitesimal change in pressure during this process. We have by the conditions of the process

$$d(u+pv) = 0. \qquad \qquad (65)$$

Since from the two laws of thermodynamics $du+pdv = Tds$, we have from (65)

$$Tds+vdp = 0, \qquad \qquad (66)$$

or

$$T\left(\frac{\partial s}{\partial T}\right)_p dT+T\left(\frac{\partial s}{\partial p}\right)_T dp+vdp = 0.$$

Now

$$T\left(\frac{\partial s}{\partial T}\right)_p = c_p; \quad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

Hence

$$c_p dT = \left(T\frac{\partial v}{\partial T}-v\right)dp,$$

or*

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{c_p} \qquad \qquad (67)$$

This gives the Joule-Thomson effect $\left(\frac{\partial T}{\partial p}\right)_h$.

For a perfect gas, $T\left(\frac{\partial V}{\partial T}\right)_p - V$ is easily seen to be zero and the Joule-Thomson effect vanishes. The porous plug experiment therefore provides a very decisive test of finding whether a gas is perfect or not.

For a gas obeying van der Waals' law it can be proved that

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{2a(V-b)^2-bV^2RT}{RTV^3-2a(V-b)^2}\cdot\frac{V}{C_p}$$

$$= \frac{1}{C_p}\left(\frac{2a}{RT}-b\right) \text{approx.} \qquad \qquad (68)$$

Hence $\frac{\delta T}{\delta p}$ is positive, *i.e.* when δp is negative there is cooling as long as $T < \frac{2a}{bR}$. At T greater than $2a/bR$ the gas becomes heated on suffering Joule-Thomson expansion. The temperature

* h stands for the total heat $u+pv$ or the enthalpy of the system.

given by $T_i = 2a/bR$ is called the temperature of inversion since on passing this temperature the Joule-Thomson effect changes its sign. It will be easily seen that $\frac{2a}{bR} = \frac{27}{4}T_c$ approximately where T_c is the critical temperature of the gas. We have already dwelt upon this point in Chap. IV. These results have been approximately verified by experiments.

36. We will analyse the Joule-Thomson effect in another way which perhaps gives a better insight into the mechanism of the phenomena. We have

$$c_p\left(\frac{\partial T}{\partial p}\right)_h = T\left(\frac{\partial v}{\partial T}\right)_p - v = -T\left(\frac{\partial s}{\partial p}\right)_T - v$$

Now
$$Tds = du + pdv.$$

$$\therefore\ c_p\left(\frac{\partial T}{\partial p}\right)_h = -\left(\frac{\partial u}{\partial p}\right)_T - \left(\frac{\partial (pv)}{\partial p}\right)_T \quad . \quad . \quad . \quad (69)$$

The first term on the right measures deviation from Joule's law while the second gives the deviation from Boyle's law, and the Joule-Thomson effect is the resultant effect due to deviations from both these laws.

Now $\left(\frac{\partial u}{\partial p}\right)_T$ is always negative, for that part of the internal energy which is due to molecular attractions always decreases with decrease of volume, *i.e.*, increase of pressure. Hence due to deviations from Joule's law alone the Joule-Thomson effect will be a cooling effect. Upon this will be superposed the effect due to deviations from Boyle's law which is a cooling effect, if $\frac{\partial (pv)}{\partial p}$ is negative (*i.e.*, before the bend in Fig. 6, p. 98) and a heating effect if $\frac{\partial (pv)}{\partial p}$ is positive.

37. Correction of Gas Thermometer.—Equation (67) can be directly utilised for giving the absolute thermodynamic scale from observations on an ordinary gas thermometer. For we have

$$T\left(\frac{\partial v}{\partial T}\right)_p = c_p\left(\frac{\partial T}{\partial p}\right)_h + v,$$

where all these quantities ought to be measured on the thermodynamic scale. In actual practice we use a gas or any other thermometer to measure this temperature which we may denote by θ and c_p' denotes the specific heat on this arbitrary scale. We have

$$c_p = \frac{dQ}{dT} = \frac{dQ}{d\theta}\frac{d\theta}{dT} = c_p'\frac{d\theta}{dT}.$$

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{dT}{d\theta}\left(\frac{\partial \theta}{\partial p}\right)_h$$

$$c_p\left(\frac{\partial T}{\partial p}\right)_h = c_p'\left(\frac{\partial \theta}{\partial p}\right)_h$$

Further $$\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial v}{\partial \theta}\right)_p \frac{d\theta}{dT}.$$

Hence (67) yields

$$\frac{dT}{T} = \frac{\left(\frac{\partial v}{\partial \theta}\right)_p d\theta}{v + c_p'\left(\frac{\partial \theta}{\partial p}\right)_h}.$$

The quantities occurring on the right-hand side can be measured on any thermometer; all that is necessary is that the same thermometer should be used in all these measurements. Further these quantities vary with temperature. As a first approximation* let us assume them to be constant. Then on integration we get

$$\log T = \log (v + \mu c_p') + \text{const.}$$

or $$T = a(v + \mu c_p'), \quad . \quad . \quad . \quad . \quad (70)$$

where μ stands for the Joule-Thomson effect $\left(\frac{\partial \theta}{\partial p}\right)_h$ and a is a constant. This shows that the thermodynamic temperature T is related to the volume of the gas in this complicated way and not only as $T \propto v$ as in the case of perfect gases. Let the thermodynamic temperatures corresponding to melting point of ice and boiling point of water be T_0 and T_{100} respectively and the corresponding volumes of the gas be v_0 and v_{100}. Then

$$\frac{T_0}{T_{100} - T_0} = \frac{T_0}{100} = \frac{v_0 + \mu c_p'}{v_{100} - v_0}.$$

Let $\alpha = \frac{v_{100} - v_0}{100 v_0}$ be the volume coefficient of expansion. Then

$$T_0 = \frac{1}{\alpha}\left(1 + \frac{\mu c_p'}{v_0}\right). \quad . \quad . \quad . \quad . \quad . \quad (71)$$

This gives the temperature of the melting point of ice on the thermodynamic scale.

The results for a few gases have been calculated and are given in Table 5. For hydrogen the Joule-Thomson cooling is $-0{\cdot}039$°C. per atm., $Mc_p = 6{\cdot}86 \times 4{\cdot}18 \times 10^7$ ergs per mole per °C, $Mv_0 = 22{\cdot}4 \times 10^3$ c.c. per mole and $\alpha = {\cdot}0036613$ per °C.

* More accurately, however, we have to integrate over short intervals.

$$\therefore \quad T = 273{\cdot}13\left(1 - \frac{{\cdot}039 \times 6{\cdot}86 \times 4{\cdot}18 \times 10^7}{10^6 \times 22{\cdot}4 \times 10^3}\right)$$
$$= 273{\cdot}13\ (1 - {\cdot}00050) = 273{\cdot}0 \text{ degrees.}$$

Table 5.—Joule-Thomson correction to the gas thermometer.

Gas.	Volume coefficient of expansion α per °C.	Mean Joule-Thomson cooling per atm.	Uncorrected temperature of melting ice $\theta_0 = \frac{1}{\alpha}$	Correction term $\frac{c_p'}{\alpha v_0}\frac{\partial \vartheta}{\partial p}$	Thermo-dynamic temperature T_0
H_2	·0036613	−0·039°C.	273·13	−0·13	273·0
Air	·0036706	+0·208	272·44	+0·70	273·14
CO_2.	·0037100	+1·005	269·5	+4·44	273·9

For air the data are most reliable and yield the value $T_0 = 273{\cdot}14°$. It will be seen that though for the various gases the melting point on the uncorrected gas thermometer ($\theta_0 = 1/\alpha$ in column 4) is much different, the melting point corrected by making use of the Joule-Thomson effect comes to about the same value, *viz.*, 273°.

To find the correction to be applied to the gas thermometer at other temperatures we must employ (70). Thus comparing (70) and (71), we have $a = 1/v_0\alpha$. Then any temperature T_1 is easily found if we measure the corresponding specific volume and the Joule-Thomson effect; for

$$T_1 = \frac{1}{v_0\alpha}\left(v_1 + c_p'\frac{\partial\theta}{\partial p}\right) . \qquad (72)$$

The gas thermometer temperature is $\theta_1 = \frac{v_1}{v_0} \cdot \frac{1}{\alpha}$, and the correction term is $\frac{c_p'}{v_0\alpha} \cdot \frac{\partial\theta}{\partial p}$. But as already mentioned on page 10 the existing data on Joule-Thomson effect are not sufficient, and the corrections are usually calculated from deviation from Boyle's law.

38. Examples.—We will now give a few examples which will illustrate the utility of the foregoing thermodynamic formulæ and will give some practice in applying them.

1. Prove that $c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p = TE\alpha^2 v$, where E is the bulk modulus of elasticity, α the coefficient of volume expansion and v the specific volume.

[We have $c_p = T\left(\frac{\partial s}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$

and $T\left(\frac{\partial s}{\partial T}\right)_v = c_v, \quad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$$\therefore \quad c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

Further from p. 240, $\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$

$$\therefore \quad c_p - c_v = -T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p^2 = TE\alpha^2 v.\ ]$$

2. Prove that $\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$.

[We have $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$. Differentiating partially with respect to T we get $\frac{\partial^2 s}{\partial T \partial v} = \frac{\partial^2 p}{\partial T^2}$. Now $c_v = T\left(\frac{\partial s}{\partial T}\right)_v$ and therefore

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\frac{\partial^2 s}{\partial v \partial T} = T\frac{\partial^2 s}{\partial T \partial v} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v\ ]$$

3. Prove that $\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$,

[Start from $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ and proceed as above.]

39. Clapeyron's deduction of the Clausius-Clapeyron Relation.—This equation was deduced on p. 262 but the method employed there is open to objection because the thermodynamic relations hold rigorously for a homogeneous substance and their extrapolation to discontinuous changes is open to question. As however the relation is important, a more rigorous deduction is given below which is due to Clapeyron.

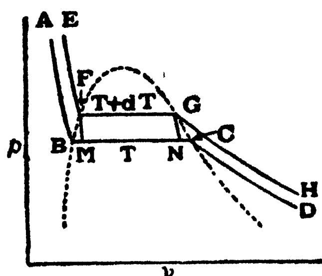


Fig. 4.—Clapeyron's deduction of the Clausius-Clapeyron relation.

Let ABCD, EFGH (Fig. 4) represent two consecutive isothermals at temperatures T and $T+dT$. From F and G draw adiabatics meeting the second isothermal at M and N. We can suppose a unit mass of the substance to be taken through the reversible Carnot cycle FGNM, for instance, allowing it to expand isothermally along FG, adiabatically along GN and compressing it along NM isothermally and then adiabatically along MF. The substance at F is in the liquid state and at G in the form

of vapour. The amount of heat taken during the cycle is therefore $L+dL$ at temperature $T+dT$. Therefore the work done during the cycle is from equation (10), p. 216, given by

$$(L+dL)\left(\frac{T+dT-T}{T+dT}\right)=\frac{LdT}{T} \text{ to the first order.}$$

Again the work done during the cycle = area of the parallelogram FGNM which is in the limit equal to FG multiplied by the perpendicular distance between FG and MN, *i.e.*, dp the increase in pressure due to increase in temperature by dT. Now FG is the change in volume due to evaporation of 1 gram of liquid and therefore equal to v_2-v_1 where v_2, v_1 denote the specific volumes of the vapour and the liquid respectively. Hence the area of the cycle is

$$(v_2-v_1)dp.$$

Equating the two expressions for area we get

$$(v_2-v_1)dp=\frac{L}{T}\,dT,$$

or

$$\frac{dp}{dT}=\frac{L}{T(v_2-v_1)} \quad . \quad . \quad . \quad . \quad . \quad (50)$$

Equation (50) is called the First Latent Heat equation or the latent heat equation of Clapeyron.

40. Specific Heat of Saturated Vapour.— A simple expression for the specific heat of saturated vapour may be deduced with the help of Fig. 3. Consider the cycle represented by the curve BFGC. The amount of heat taken by the substance during its passage from B to F is $c_{s_1}\,dT$ and that during the path FG is $L+dL$. On the other hand the substance gives back heat equal to $c_{s_2}\,dT$ during the path GC and equal to L during the path CB. c_{s_1} denotes the specific heat of the liquid in contact with vapour, and c_{s_2} the specific heat of the vapour in contact with liquid (specific heat of saturated vapour). The total amount of heat taken during the cycle BFGC is

$$c_{s_1}\,dT+L+dL-c_{s_2}\,dT-L,$$

and this must in the limit be equal to the area FGNM, which is equal to $\frac{LdT}{T}$ as proved in the last section.

$$\therefore\quad c_{s_1}\,dT+L+dL-c_{s_2}\,dT-L=\frac{LdT}{T},$$

or

$$\frac{dL}{dT}-\frac{L}{T}=c_{s_2}-c_{s_1} \quad . \quad . \quad . \quad . \quad . \quad (73)$$

This is called the latent heat equation of Clausius or the Second Latent Heat equation.

It may be noted that c_{s_1} is neither the specific heat at constant pressure nor the specific heat at constant volume. Here the liquid and the vapour always remain in contact and therefore the vapour always remains saturated. Both the pressure and the volume are so varied that the condition of saturation is always satisfied. It is easily seen that c_{s_1} does not appreciably differ from c_{p_1} the specific heat at constant pressure, for the effect of pressure is too small to bring about any considerable change in the state of the liquid. c_{s_1} can therefore be put equal to c_{p_1}. We can now calculate the value of c_{s_2} from equation (73). For water at 100°C.

$$\frac{dL}{dT} = -0{\cdot}64 \text{ cal. gm.}^{-1}{}^\circ\text{C}^{-1};\ L = 539 \text{ cal. gm.}^{-1}$$

$$T = 373^\circ;\ c_{p_1} = 1{\cdot}01 \text{ cal. gm.}^{-1}{}^\circ\text{C}^{-1}$$

$$\therefore\quad c_{s_2} = 1{\cdot}01 - 0{\cdot}64 - \frac{539}{373} = -1{\cdot}07 \text{ cal. gm.}^{-1}{}^\circ\text{C}^{-1}.$$

Thus the specific heat of saturated water vapour at 100°C. comes out to be a negative quantity. This is rather a paradoxical result but at the same time perfectly true. In Chapter II we have seen that the specific heat may vary from $+\infty$ to $-\infty$ depending entirely upon the external conditions. In the present case the condition of saturation has to be always satisfied. Now saturated water vapour has a pressure of 760 mm. at 100°C. and 787·6 mm. at 101°C. *i.e.*, the specific volume of saturated water vapour decreases as the temperature rises. This is so with all vapours. Hence when saturated water vapour at 100°C, is heated to 101°C. at constant pressure it becomes unsaturated, but since the condition of saturation has to be satisfied, it must be compressed till the pressure becomes 787·6 mm. This compression generates heat, and in the case of water at 100°C. the heat generated is so great that some of it must be withdrawn in order that the temperature may not rise above 101°. The net result in this case is that heat must be withdrawn from and not added to the system during the whole operation. Thus we explain physically why the specific heat of saturated vapour sometimes becomes negative.

The same idea can be expressed mathematically. We have

$$\left(\frac{ds_2}{dT}\right)_{\text{sat.}} = \left(\frac{\partial s_2}{\partial T}\right)_p + \left(\frac{\partial s_2}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_{\text{sat.}}$$

where $\left(\frac{dp}{dT}\right)_{\text{sat.}}$ refers to the condition of saturation being satisfied.

Or.

$$c_s = c_p - T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{dp}{dT}\right)_{\text{sat.}}$$

Now for all vapours $\left(\frac{\partial v}{\partial T}\right)_p$ is positive and hence c_s is always less than c_p and may even become negative.

From these considerations it will be seen that saturated steam must become superheated by adiabatic compression, *e.g.*, water vapour at 100°C. and 760 mm. pressure, when compressed suddenly to 787 mm. would be heated by 2·1°C., and hence become superheated; in other words, when the temperature of saturated steam is raised it *gives out* heat. Conversely, when it is allowed to expand adiabatically, say, from 787 mm. to 760 mm., the temperature would fall by 2·1°C., *i.e.*, to 98·9°, and hence it would be supercooled, and partial condensation may occur. For certain vapours such as saturated ether vapour, the work done in compressing the substance is not so great and the specific heat is positive. These do not become superheated by adiabatic compression.

These conclusions were experimentally verified by Hirn in 1862. He allowed steam from boilers at a pressure of five atmospheres (temperature about 152°C) to enter a long copper cylinder fitted with glass plates at its ends. When all the air and condensed water had been driven out, and the cylinder had attained the temperature of the steam, the taps in the supply and the exit tubes were closed, and the vapour when viewed from the ends looked quite transparent. The exit tube was next suddenly opened and the vapour expanded adiabatically and a dense cloud was observed inside the cylinder. The cloud however soon disappears as the cooled vapour rapidly absorbs heat from the walls of the cylinder which are at 152°C. No such condensation was observed in experiments with ether vapour.

41. The Triple Point.—If we now plot the saturation value of p against T we get a curve OA (Fig. 5) the slope at every point of which will be given by

$$\frac{dp}{dT}=\frac{L_1}{T(v_g-v_l)},$$

where L_1 is the latent heat of vaporisation, and v_g, v_l denote the specific volume at the temperature considered.

To fix our ideas let us consider the case of water. When the temperature is reduced to 0°C. water freezes and we get ice. But ice has also a definite vapour pressure which has been measured. The vapour pressure curve of ice may be represented by the line OB, the slope at every point of which will be given by

$$\frac{dp}{dT}=\frac{L_2}{T(v_g-v_s)}$$

where L_2 is the latent heat of sublimation.

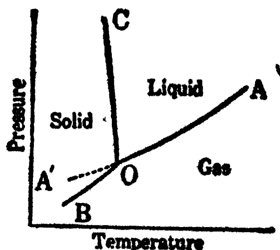


Fig. 5.—The triple point.

Similarly for the phenomenon of melting, the curve OC represents the relation between pressure and temperature, and the slope at any point is given by

$$\frac{dp}{dT}=\frac{L_3}{T(v_l-v_s)},$$

where L_3 is the latent heat of fusion. We have already seen on p. 262 that for ice $\frac{dp}{dT}=133\times10^6$ dynes cm.$^{-2}$ °C^{-1}, *i.e.*, the curve should be almost vertical.

For substances which contract on solidification the slope of OC will be positive. The three lines OA, OB, OC are respectively called *vaporization line*, *sublimation line* and *fusion* line, and in the particular case of water they are called steam line, hoar-frost line and ice line respectively.

Consider the substance in the state represented by any point Q above the line OA. It will be noticed that the pressure of the substance in this state is greater than that which will correspond to the saturated vapour pressure at that temperature and which is given by the intersection of OA with the ordinate drawn from Q. At this higher pressure represented by Q, therefore, the substance cannot boil at this temperature as boiling point is raised by pressure, and must therefore exist as liquid. Thus the region above OA represents liquid state. Similarly for points below OA the corresponding vapour pressures are too low and the substance must exist as gas. Similarly above OB the substance must exist as solid and below it as gas. Again above any point in OC due to the pressure being larger than that corresponding to the ice line, ice will melt and therefore the region above OC represents water, and that below represents ice.

It can be easily shown that these three curves must meet in a single point which is called the triple point. For, if the curves do not meet at a point, let them intersect each other forming a small triangle ABC (Fig. 6.). Then since the space ABC is above AB it must represent the liquid region, but it is below AC and must therefore represent gas, and is also below BC and must therefore also represent solid. Thus the region ABC must simultaneously represent the solid, liquid and gaseous states. Evidently it is impossible to satisfy these mutually contradictory conditions and the only conclusion to be drawn is that such a region does not exist. In other words, all the three curves meet in a single point.

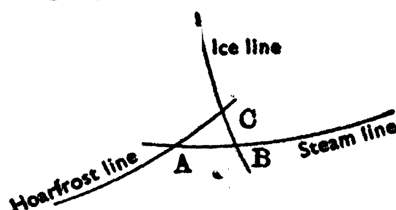


Fig. 6.—Impossible intersections of ice, steam and hoarfrost lines.

The coordinates of the triple point can be easily calculated from the consideration that at this point, the vapour pressure of water

is equal to the melting pressure of ice. The vapour pressure of water at 0°C is 4·58 mm. and at 1°C, 4·92 mm. Thus the vapour pressure rises by 0·34 mm. per degree, and therefore, if t is the triple point the vapour pressure p at the triple point is given by

$$p = 4{\cdot}58 + 0{\cdot}34\, t. \qquad (74)$$

The melting pressure of ice at 0°C is 760 mm. and the change of melting point with pressure is 0·0075°C per atm. Therefore the melting point t at the pressure p will be

$$t = 0{\cdot}0075 - \frac{0{\cdot}0075}{760} p. \qquad (75)$$

Solving (74) and (75) we get

$$t = 0{\cdot}007455°\text{C and } p = 4{\cdot}5824 \text{ mm.}$$

It will be apparent that since the change in vapour pressure is too small in comparison to the change in melting pressure, it is useless to go through the complicated calculation given above and we can simply assume that $p = 4{\cdot}58$ mm approximately (as t will be very near 0°C) and calculate the corresponding melting temperature. Thus

$$t = 0{\cdot}0075 - \frac{0{\cdot}0075 \times 4{\cdot}58}{760} = 0{\cdot}007455°\text{C}.$$

The coordinates of the triple point are therefore t = ·0075°C., p=4·58 mm. At this point three phases (solid, liquid and vapour) co-exist.

It was formerly supposed that the curves OA, OB are continuous. It was first proved by Kirchhoff that this is not so, for according to (50)

$$\frac{dp}{dT} \text{ for OA at 0°C.} = \frac{L}{T(v_2 - v_1)}$$

$$= \frac{607 \times 4{\cdot}18 \times 10^7 \times 760}{273 \times 21 \times 10^4 \times 10^6}$$

$$= 0{\cdot}337 \text{ mm. per degree.}$$

$$\frac{dp}{dT} \text{ for OB (sublimation)} = \frac{687 \times 4{\cdot}18 \times 10^7 \times 760}{273 \times 21 \times 10^4 \times 10^6}$$

$$= 0{\cdot}376 \text{ mm. per degree.}$$

The dotted curve OA′ is merely the continuation of OA. It represents the vapour pressure of supercooled liquid. At −1°C. we have vapour pressure of liquid − vapour pressure of solid = ·04 mm. of mercury. This has been verified by the experiments of Holborn, Scheel and Henning.

Books Recommended:

1. Fermi, *Thermodynamics.*

2. Planck, *Treatise on Thermodynamics.*

3. Hoare, *Thermodynamics.*

4. Smith, *The Physical Principles of Thermodynamics* (1952), Chapman & Hall.

5. Epstein, *Text-Book of Thermodynamics*, John Wiley.

CHAPTER XI

RADIATION

1. Introduction.—Even when a heated body is placed in vacuum, it loses heat. In this case no heat can be lost by conduction or convection since matter, which is absolutely essential for both these processes, is absent. In such cases we say that heat is lost by 'Radiation.' To differentiate this process from conduction, it is enough to note that copper and wood, which are so much different in their conducting powers, cut off radiation equally well when placed between the hot body and the observer.

Now heat has been shown to be a form of energy, and the propagation of heat by radiation consists merely in a transference of energy. But the radiant energy in the process of transference does not make itself evident unless it falls on matter. When it falls on matter and is absorbed, it is converted to heat and can be thereby detected.

Let us now study some of the properties of radiant energy. For this purpose we require a source of heat as radiator and some instrument to measure the emitted radiation. As emitter Leslie employed a hollow metal cube filled with hot water, whose sides could be coated with different substances. The cube is so made that it can be rotated about a vertical axis. Such a cube is called a Leslie cube and is shown in Fig. 1. For measuring the radiation the early experimenters employed a differential air-thermometer or a thermopile which are described in the next section.

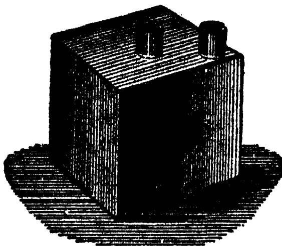


Fig. 1.—Leslie cube.

2. Some Simple Instruments for Measuring Radiation.— Leslie, one of the earliest workers, used a *differential air-thermometer* which is now only of historical interest. This consists of two equal bulbs A and B (Fig. 2) containing air and communicating with each other through a narrow tube bent twice at right angles and containing some non-volatile liquid like sulphuric acid. When the bulbs are at the same temperature the liquid stands at the same height in both the columns C and D, but if one of the bulbs A is heated the level of the liquid falls in the column C and rises in the column D. By noting the difference in level of the two columns the difference in temperature of the bulbs can be easily calculated.

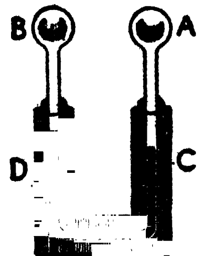


Fig. 2.—Leslie differential air thermometer.

Melloni was the first to introduce *thermopiles* for the measurement of radiant energy. In its original form,

Melloni's thermopile consisted of a number of bismuth and antimony rods, placed alternately with their ends joined, as indicated in Fig. 3. The left face forms the hot junction, and the right the cold junction. The antimony bars are shaded and the bismuth bars are left clear. The current flows across the hot junction from bismuth to antimony.

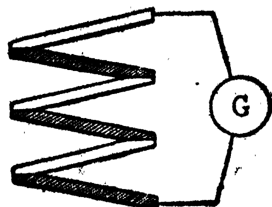


Fig. 3.—Principle of the thermopile.

In an actual thermopile a large number of pairs is employed. The bars are arranged in the form of a cube such that all the hot junctions are at one face and the cold junctions at the opposite face. Such a cube is shown in Fig. 4. The near face is the hot junction and is coated black. The thick lines denote the insulating material, generally mica. between the different layers, and the thin lines denote the soldered junctions. The current enters at A, flows across the soldered junction at the near face into the antimony bar, and so on. It enters the next layer at B on the cold face and so on. Finally the current leaves the thermopile at C. A thermopile mounted for use is shown in Fig. 5. The blackened face is provided with a conical protector to protect it from stray radiations, while the cold face is covered with a metallic cap. Another cap serves to protect the hot junction when not in use.

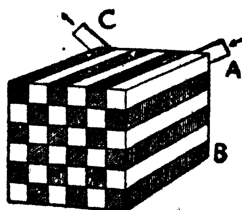


Fig. 4.—The thermopile.

Other types of radiometers are described in sections 21-24.

3. Properties and Nature of Radiant Energy.— With the aid of these simple apparatus, it can be demonstrated that Radiant Energy and Light obey identical laws and have identical properties. We mention some of the points of resemblance.

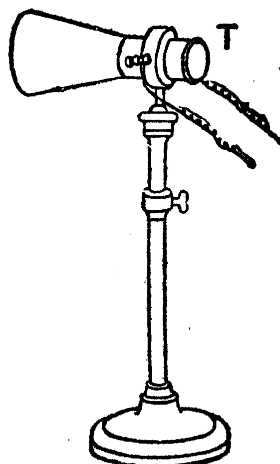


Fig. 5.—The thermopile (mounted).

(i) Radiant energy, like light, can travel through vacuum, for we are able to receive heat from a hot electric glow lamp though it is highly evacuated. Even when a feeble current passes through the filament which is not sufficient to make the filament glow, the thermal radiation coming from the latter can be detected by a sensitive thermopile.

(ii) Radiation, like light, travels in straight lines.—This can be easily seen for the heat coming from a flame can be easily cut off by interposing

a screen just sufficient to prevent the light coming from it. On replacing the flame by a hot non-luminous source, no heating effect can be detected by a thermopile. The exact geometrical shape of the image can be verified by cutting out a cross from the screen and holding close to it a piece of wood coated with paraffin wax. The wax will melt in the shape of a cross.

(iii) Radiation travels with the velocity of light.—This follows from the observation that the obstruction of the radiation from the sun during a total solar eclipse is immediately accompanied by a fall of temperature.

(iv) Radiant energy follows the law of inverse square like light.—This may be experimentally proved by the simple arrangement shown in Fig. 6. A is a vessel containing hot water and having one surface B plane and coated with lamp-black. S is a thermopile. It will be found that if we move the thermopile to another position S′ (say double the previous distance), the deflection of the galvanometer connected to it will be unchanged. Now the area of the surface of B from which radiation can reach the thermopile is increased four times, and as the amount of radiation reaching the pile remains the same, intensity of radiation must be reduced to ¼th, i.e., the intensity of radiation varies inversely as the square of the distance.

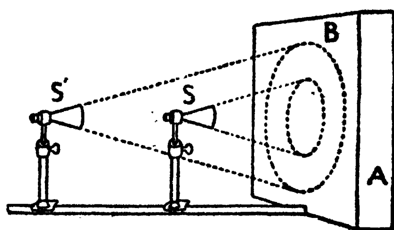


Fig. 6.—Verification of inverse square law.

(v) Radiation obeys the laws of reflection of light.—This can be easily verified by placing two parabolic mirrors A and B at some distance apart with their axes in the same line (Fig. 7). A luminous source placed at the focus of A produces an image at the focus of B. If we replace the luminous source by a hot non-luminous one, say a Leslie cube, and put a piece of tinder at the other focus, the tinder is ignited. This shows that heat and light travel along the same path and hence obey identical laws. In fact all the laws and results of geometrical optics are applicable to it.

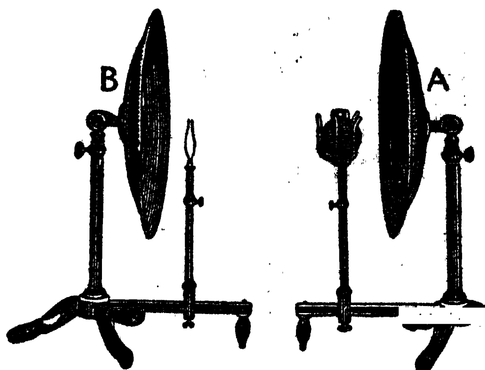


Fig. 7.—Verification of laws of reflection for radiation.

(vi) Radiant energy suffers refraction, like light—A spectrum may be obtained by refraction through a prism (sec. 29).

(vii) Thermal radiation exhibits the phenomena of interference and diffraction.—Diffraction can be easily observed with the help of a concave grating or by employing a transmission grating made of a number of equidistant parallel wires.

(viii) Thermal radiation can also be polarised in the same way as light by transmission through a tourmaline plate. This can be shown by the following experiment:—Arrange that light from an incandescent lamp traverses two similar plates of tourmaline. On rotating one of the plates the image will be found to vanish. Replace the lamp by a Leslie cube. Now a thermopile placed in the position occupied by the image will record no deflection ; if however one of the plates be rotated a deflection will be observed.

4. Identity of Radiant Energy and Light—Continuity of Spectrum.— All these observations lead us to the conclusion that radiant energy is identical with light. As we shall see presently, Radiation or Radiant Energy is the general and more expressive term, light (or rather visible light) being only a kind of radiant energy which has the distinctive power of affecting the retina of the human eye, and thus producing the sensation of colour. But like other kinds of radiant energy light is also converted to heat when it is absorbed by matter.

The identity of light and radiant energy can further be seen from the following experiments:—

(*i*) When we produce a spectrum of the sun by means of a prism, it is terminated on one side by the red, and on the other side by the violet. But it can be easily seen that these limits are only apparent, and are due to the fact that the human eye is a very imperfect instrument for the detection of radiation. W. Herschel* (1800) placed a blackened thermometer bulb in the invisible part beyond the red, and found that the thermometer recorded a rise in temperature. The rise in temperature was observed also when the thermometer was placd in the visible region. Thus W. Herschel discovered the infra-red part of the solar spectrum, and showed that it was continuous with the visible spectrum.

The source of radiation in this case is the sun, which may be regarded as an intensely hot body. But it may be substituted by any sufficiently hot substance, say a piece of burning coal ; the positive crater of the arc, or a glowing platinum wire. Only in these cases the intensity of radiation is not great, and the spectrum does not extend so far towards the violet.

(ii) Production of light by heating.—A very simple experiment will suffice to bring out the point which has been just mentioned. Suppose we take a piece of blackened platinum wire and pass through

* William Herschel (1738—1822) was born at Hanover but settled in England. He first worked as a musician and later became an astronomer. He discovered the planet Uranus in 1781 and later discovered the infra-red radiations.

it a continuously increasing current. The function of the current is simply to heat the wire. We find that it becomes warm, and sends out radiant energy. If a thermopile be held near it, the galvanometer connected to it will show a deflection. When a slightly stronger current is passed the wire begins to glow with a dull red light. This shows that the wire is just emitting red radiation of sufficient intensity to affect the human eye. Accurate observations† show that this takes place at about 525°C (*Draper point*). With increasing temperature, the colour of the emitted radiation changes from dull red to cherry red (900°C), to orange red (1100°C), to yellow (1250°C), until at about 1600°C it becomes white. Thus the temperature of a luminous body can be roughly estimated visually from its colour. Such a colour scale of temperature is given in the chart on pp. 25-26. This shows that *shorter waves are emitted by a heated body in sufficient intensity only with increasing temperature.* Vice versa, we may argue that when the temperature of the wire is below the Draper point, it is emitting longer waves than the red, but these waves can be detected only by their heating effect.

Radiant Energy or Radiation is thus a more general name for Light. It can be of any wave-length from 0 to ∞ as illustrated in the chart on pages 283-284. Light forms less than 3/4ths of an octave on the scale.

Explanation of the Chart.—We are using here the logarithmic scale, i.e., log λ is plotted along the vertical line. Thus (-5) on the scale indicates that the wavelength is 10^{-5} cm., (-2) indicates that $\lambda = 10^{-2}$ cm. As shown in the chart visible light extends from 7×10^{-5} cm. (red) to about 4×10^{-5} cm. (violet). The infra-red part was discovered by W. Herschel and the extension towards the longer wavelength side is chiefly due to the reststrahlen method of Rubens and Nichols. These rays are detected chiefly by the thermopile, for ordinary photographic plates are not sensitive beyond the green. Above green, panchromatic plates may be used, but they are also not sensitive beyond 8000 Å. U. Beyond this plates dipped in dycyanine or neocyanine may be used up to 10000 Å. U. Recently photographic plates sensitive upto 20000 Å. U. have been placed on the market.

The Hertzian waves are produced by purely electromagnetic methods (due to oscillation of current in an inductance-capacity circuit) and were first discovered by Hertz in 1887. Marconi applied them for wireless transmission (1894). Waves used for this purpose are generally 10—500 metres in length, though waves of about 10 km. length have been used in the past. These long electromagnetic waves differ from the light waves only in their wavelength, and attempts have been made to get shorter and shorter waves by purely electromagnetic methods so that one can pass continuously to the

† According to a recent experiment by Babcock, persons who have rested their eyes in the dark carefully, can detect radiation even from a body heated to about 400°C.

ELECTROMAGNETIC WAVES

Wavelength	Log λ cms	Radiation	Generation	Detection and Analysis	Discoveror
10^{-11} Siegbahn unit	-11	Hard γ rays	Nuclear Reactions	Pair production Compton effect	
	-10	γ-rays	Radioactive Disintegration	Photo-electric method	
·06A.U.	-9	X-rays Hard	Bombardment of metal targets by electrons	Crystals & Photography or Ionisation chamber	Röntgen (1895) Laue (1912)
10^{-8} Ångström unit	-8	Medium		Fluorescence	
	-7	Soft		Reflection Grating (vacuum)	Compton (1925) Thibaud (1926)
136 A.U.	-6		Vacuum Spark	Photogr-aphy	Millikan (1919) & Lyman (1906)
$1·0\times10^{-5}$	-5	Ultra-violet		Prisms; Vacuum grating	Schumann (1890) Ritter (1802)
4×10^{-5} 8×10^{-5}		VISIBLE Violet Red	Spark. Arc Flame	Glass; Quartz; Fluorite	NEWTON
μ	-4				Herschel (1840)
			Heating	Wire gratings & Thermo-couples	
	-3	Infra-red		Residual ray Method	Rubens & Nichols (1896)
1 mm	-2	Hertzian waves		Focal Isolation	Wood (1912)
·4 mm					Nichols & Tears (1924)
	-1	(Short)	Spark gap	Coherer	
4 mm	0				Bose (1902)

ELECTROMAGNETIC WAVES (Contd.)

Wavelength	Log λ	Radiation	Generation	Detection and Analysis	Discoveror
cms	-1				
	0		Spark gap discharge		
	+1	Hertzian waves	Triode valve Oscillator	Radar (Micro-wave Technique)	
1 metre	+2				Hertz (1887)
	3	Short-wave Broadcasting		Wireless Methods	
100 metres	4				
		Long-wave Broadcasting			
	5				
10^4 metres	6	Hertzian waves ↓			
	7	No upper limit			
	8				

long infra-red rays. The limits successively reached are due to Lebedew, Lampa, Sir J. C. Bose (4 mm.) and the gap between electromagnetic waves and heat waves has been completely bridged by the work of Nichols and Tear, Arcadiewa, and others. During World War II the technique of production of waves of length from a few metres to a few centimetres has undergone a complete revolution by the discovery of magnetron and klystron tubes used for Radar.

The ultraviolet part (rays shorter than the last visible $\lambda = 3800$) was discovered by W. Ritter in 1802. He found that a photographic plate was affected even beyond the visible limit. Glass spectrographs usually give lines as far as $\lambda = 3400$, after which either uviol glass (limit $\lambda = 2800$) or quartz prisms should be used. At about $\lambda = 2200$, the gelatine used in the photographic plates begins to absorb. Schumann was the first to prepare plates without gelatine and open up what is called the Schumann region. Below $\lambda = 1850$ Å.U. quartz begins to absorb heavily, and Schumann therefore used fluorite-spectroscopes. Beyond $\lambda = 1400$, air absorbs heavily, and the whole operation of producing light and photographing the spectrum must be done in vacuum. The pioneer in this field was Th. Lyman of Harvard, who was able to photograph lines as far as $\lambda = 600$. In this region gratings have to be used for producing the spectrum.

X-rays were shown by M. Laue in 1912 to be light waves of extremely short wavelength 10^{-8} cm., *i.e.*, about 1000 times shorter than ordinary light. He used a crystal as diffraction grating. The shortest X-rays measured by the crystal method has the wave-length = ·05 Å.U. γ-rays, obtained in radioactive disintegration of the nuclei of atoms, are still shorter, viz., from 10^{-9} to 10^{-10} cm. in wavelength.

The gap between the Lyman region (600 Å. U.) and the soft X-ray region (about 20 Å. U.) has been gradually bridged by the works of Millikan and Bowen, Compton, Thibaud and others. Millikan and Bowen used ordinary vacuum spectrographs with diffraction gratings. Their source of light was condensed vacuum spark. For wavelength in this region, crystal gratings have their spaces too small, while the ruled gratings have their spaces too large. Compton instituted the method of obtaining spectra in this region with the aid of coarse grating at glancing angle (see M. N. Saha and N. K Saha, *Treatise on Modern Physics*, Vol. I, p. 278).

Since radiant heat and light are identical, all the laws and theorems of Optics and Spectroscopy can be applied to the study of radiation. But in this chapter, we shall deal with the subject only as far as it is connected with heat. We shall first enter into a preliminary discussion regarding the passage of radiation through matter.

5. Fundamental Radiation Processes.— Every hot body emits radiation from its surface which depends upon the nature of the surface, its size and its temperature. This is known as *emission*. When the emitted radiation falls on matter, a part is *ref*

regularly or irregularly (diffuse), another part is *absorbed* while the remainder is *transmitted*. The coefficients of reflection, absorption and transmission are connected by the relation

$$r+a+t=1,$$

where r = fraction of total energy reflected
a = ,, ,, ,, ,, absorbed
t = ,, ,, ,, ,, transmitted.

From our common experience, we can define certain substances with limiting properties as regards their behaviour towards radiant energy.

Perfectly Black Bodies.—For such bodies, $r=0$, $t=0$, $a=1$. Lamp-black is the nearest approach to such a body. Apparently, it neither reflects nor transmits the light which falls on it, absorbs all, and hence appears black. But the perfectly black body is only an ideal conception, for even lamp-black is found to transmit light of long wavelength. It absorbs about 96% of visible light, platinum black absorbs about 98%.

6. Theory of Exchanges (Prevost—1792).— Prior to 1792 the ideas regarding emission of radiant energy were very much confused. People used to talk of hot radiations and cold radiations. A block of ice was supposed to emit cold radiations because it produced a sensation of cold. Prevost of Geneva was the first to recognise that this was a loose way of talking. He said that substances at all temperatures emit radiant energy, but the amount increased with the temperature and is not affected by the presence of surrounding bodies. The rise or fall of temperature which is observed in a body is due to its exchange of radiant energy with surrounding bodies. This is known as *Prevost's Theory of Exchanges.*

Thus when we stand near a fire, we feel the sensation of warmth, because our body, *which is also a radiator*, is receiving more energy from the fire than it is losing by its own radiation. When we stand near a block of ice, we feel a sensation of cold because our body being at about 37°C loses more energy by radiation than it receives from the ice, which is at a much lower temperature, *i.e.*, 0°C. These considerations are quite general, and may be applied to all similar phenomena.

A body will cease to emit radiation only when it is at the absolute zero of temperature (−273°C).

7. Laws of Cooling.—When we have already recognised that every substance emits radiation by virtue of its temperature, it becomes necessary to investigate how its emission varies with the temperature and the nature of the surface. In this section we shall confine our attention to the effect of temperature, both of the substance and the surroundings. Newton was the first to study systematically the loss or gain of heat by a body placed in a given enclosure. The experiments can be most simply performed by heating a large-

bulbed mercury thermometer and enclosing the bulb in an evacuated flask, the walls of which are blackened inside and are further maintained at a fixed temperature by means of a suitable bath. The rate of fall of temperature of the thermometer gives the rate of cooling. It was found that if we plot the rate of cooling $-\frac{d\theta}{dt}$ as ordinate against the excess of temperature as abscissa, the curve is a straight line, or in other words,

$$-\frac{d\theta}{dt} = k(\theta - \theta_0), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ_0 is the temperature of the enclosure, *i.e.*, the rate of cooling is proportional to the excess of temperature of the substance above the surroundings. This is *Newton's law of cooling*. The law holds when the temperature difference is not large. Even the earlier experiments showed considerable deviations from the law when the temperature difference exceeded 40°C.

In order to find out a law which will hold for all differences of temperature, an elaborate series of experiments were performed by Dulong and Petit who found that their results were given by a formula of the form

$$-\frac{d(\theta - \theta_0)}{dt} = k(a^{\theta} - a^{\theta_0}), \quad . \quad . \quad . \quad (2)$$

where a is a constant and k depends upon the nature of the emitting surface, and θ, θ_0 denote respectively the temperatures of the emitting surface and the surroundings.

Stefan* showed later that the results of Dulong and Petit may be represented by the equation

$$-\frac{dT}{dt} = a(T^4 - T_0^{\,4}), \quad . \quad . \quad . \quad . \quad (3)$$

where a is a universal constant, and T and T_0 the absolute temperatures of the body and its surroundings; or in other words, the emissive power of a substance varies as the fourth power of the absolute temperature. This is Stefan's law and can be deduced from theoretical considerations (*vide* sec. 26). It is therefore the correct law of cooling for black bodies.

Newton's law of cooling can be easily deduced from Stefan's law when the temperature difference is small. Thus if the body at temperature $T + \delta T$ is placed in an enclosure at temperature T°K, the rate of loss of heat per second by unit area of the body is

$$\sigma(T + \delta T)^4 - \sigma T^4$$

$$= \sigma T^4 \left(1 + \frac{\delta T}{T}\right)^4 - \sigma T^4 = 4\sigma T^3 \delta T$$

neglecting higher powers of δT. It is thus proportional to the temperature difference δT.

* Josef Stefan (1835—1893) was Professor of Physics in Vienna. He discovered the law known by his name.

Generally for rough work in the laboratory Newton's law of cooling is employed for correcting for heat loss even when the body is not suspended in vacuum. As shown in Chap. VIII, § 30, if cooling takes place by natural convection in air, Newton's law does not hold. In accurate work the exact rate of cooling should be observed and not computed.

Exercise.—A body cools from 50°C to 40°C. in 5 minutes when its surroundings are maintained at 20°C. What will be its temperature after a further 5 minutes? Assume Newton's law of cooling to hold.

$$\left[\frac{d\theta}{dt} = -k(\theta-20); \qquad \therefore \quad \log\,(\theta-20) = -kt+C.\right.$$

Now for $t = 0,\ \theta=50;\quad t = 5,\ \theta = 40;$
$t = 10,\ \theta = \theta_x$(to be determined).

$$\therefore \quad C = \log_e\ 30;\ k = -\frac{1}{5}\log_e\frac{20}{30}$$

$$\left.\therefore \quad \log_e\frac{\theta_x-20}{30} = 2\ \log_e\frac{20}{30} \text{ whence } \theta_x=33{\cdot}3\,^\circ\text{C.}\right]$$

8. Emissive Power of Different Substances—Preliminary Experiments.— Having made an experimental study of how the emissive power varies with temperature, let us find how the emissive power varies with the nature of the surface of the emitting body. For this purpose one face of the Leslie cube is coated with lamp-black while another face is coated with the substance whose emissivity is to be found. The radiation from both these surfaces can be allowed to fall alternately on a thermopile placed at some distance. The ratio of the deflections recorded by the thermopile in the two cases gives the ratio of the emissive powers of the two substances. In this way the relative emissivities of different substances were determined. The expriments were performed by Leslie, Melloni and others.

9. Reflecting Power.— The reflecting power of different substances can be very simply found by allowing the radiation from a Leslie cube to fall on a reflecting surface and the reflected radiation to fall on a thermopile. Next the thermopile is placed at the position occupied by the reflecting surface. The ratio of the deflections in the two cases gives the reflecting power. This however varies with the wavelength of radiation employed, and as earlier workers did not employ monochromatic radiation, their results are not of much value.

10. Diathermancy.— Diathermancy with regard to heat is analogous to transparency in the case of light. Substances which allow radiation to pass through them are called *diathermanous*, while those which do not, are called *athermanous*. The early experiments in this direction were performed by Melloni and Tyndall. Direct radiation from a Leslie cube fell on a thermopile producing deflection; next the experimental substance was introduced and the deflection observed. The ratio of the two deflections gives the diathermancy

or transmission coefficient of the substance. Solids, liquids and gases were treated in this way. The best diathermanous solids are rock-salt (NaCl), sylvine (KCl), quartz, fluorite and certain other crystals. Pure air is highly diathermanous, but water vapour and carbon dioxide show marked absorption.

11. Absorption.— For studying the absorption of solids Melloni took a copper disc and coated one face with lamp-black and the other face with the experimental substance. The copper disc was placed between the Leslie cube and the thermopile, the lamp-black surface facing the thermopile. The plate will assume a steady temperature T. The heat radiated per unit area of the plate is

$$H = (E - E')T,$$

where E and E' denote the emissivity of lamp-black and of the substance. Now this must equal the radiation which it absorbs. The thermopile reading gives ET and therefore E. Knowing E and E' we get H, the energy absorbed. In this way the absorptive power of different substances could be compared. For gases a sensitive arrangement was employed.

The terms diathermanous or athermanous lack in scientific precision. Every substance ought to be defined, so far as its transmitting or absorbing properties are concerned, with respect to a particular wavelength. In the above experiments monochromatic radiations were not employed. The whole subject is now studied as a branch of physical optics under the head 'dispersion and reflection' with which it is intimately connected.

12. Relations existing between the different Radiation Quantities.— The foregoing experiments however show that at the same temperature a lamp-black surface emits the maximum energy while a polished surface emits very little energy. It was further found that radiating and absorbing powers vary together; that *good radiators are good absorbers and poor reflectors, while poor radiators are poor absorbers.* Lamp-black is opaque to radiation but allows radiation of very long wavelength to pass through it.

A very simple experiment devised by Ritchie demonstrates vividly the relation between emissive and absorptive powers of a body. A Leslie cube AB, which is a hollow metallic vessel and can be filled with liquid at any temperature, is placed between the two bulbs of a differental air thermometer (Fig. 8). The face A of the cube and the bulb D are coated with lamp-black while the face B and the bulb C can be coated with a layer of the substance whose emissivity is to be investigated, say powdered cinnabar. By filling the cube with a hot liquid the index was not found to move, and hence the amounts of energy received by C and D are equal. If e denotes the

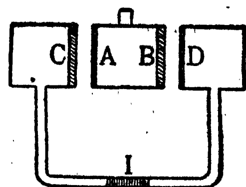


Fig. 8.—Ritchie's experiment.

amount of heat emitted by the substance and a its absorptive power, while E and 1 denote the corresponding quantities for lamp-black, we have

$$e = aE,$$

or
$$\frac{e}{E} = a. \qquad \qquad (4)$$

Now e/E may be called the coefficient of emission of the substance, and hence the relation shows that the coefficient of emission is equal to the absorptive power. It will be seen that the effect of temperature upon the coefficient of emission has been neglected here. Nevertheless the experiment shows at least qualitatively that the coefficients of emission and absorption vary in the same manner from one substance to another.

These ideas were further developed and made more precise by Kirchhoff and Balfour Stewart. Before proceeding further it is however necessary to define the concepts used in Radiation with more rigour. We now proceed to do this in the next section.

13. Fundamental Definitions.— If a body is heated it radiates heat from its surface in all directions, which comprises waves of all lengths. The nature of radiation depends on the physical properties of the body. We denote by $e_\lambda\, d\lambda$ the amount of radiation measured in ergs emitted normally per unit area per unit solid angle per second within the wavelengths λ and $\lambda + d\lambda$. We shall call e_λ the *emissive power* of the body. Similarly if dQ_λ be the amount of radiant energy falling on the body in the form of radiation (λ to $\lambda + d\lambda$) and a fraction $a_\lambda dQ_\lambda$ of it is absorbed by the body and converted into heat, then a_λ is called the *absorptive power* of the body for these rays (λ to $\lambda + d\lambda$). For black bodies $a_\lambda = 1$ for all wavelengths, but for other substances a_λ depends on the physical nature of the body.

14. Kirchhoff's Law.— In sec. 12 we saw that emission and absorption vary together. In 1859, Kirchhoff* deduced an important law which may be stated as follows :—

At a given temperature the ratio of the emissive power to the absorptive power is the same for all substances and is equal to the emissive power of a perfectly black body.

Though this law was first recognised by Balfour Stewart, Kirchhoff was the first to deduce it from thermodynamical principles, and apply it in all directions. It is therefore usually known as Kirchhoff's law.

We have considered here the total emission regardless of wavelength but the same relation holds for each wavelength separately. Thus for radiations of the same wavelength and the same tempera-

* Gustav Robert Kirchhoff (1824—1887), born at Königsberg, became Professor of Physics at Breslau and Heidelberg. He is noted for his discoveries in spectrum analysis and the radiation law bearing his name.

ture, the ratio of the emissive and adsorptive powers for all bodies* is the same and equal to the emissive power of a perfectly black body. This also holds for each plane-polarised component of any ray.

Kirchhoff's own proof of the law is however very complicated and has somewhat fallen into disuse. We shall give in sec. 19 a much simplified proof of the law. But before doing so let us consider its applications.

15. Applications of Kirchhoff's Law.—The law embodies two distinct relations, a qualitative and a quantitative one. Qualitatively, it implies that if a body is capable of emitting certain radiations it will absorb them when they fall on it. Quantitatively, it signifies that the ratio is the same for all bodies.

Various experimental proofs and observations may be cited in support of the qualitative relation. If a piece of decorated china is heated in a furnace to about 1000°C and then taken out suddenly in a dark room, the decorations appear much brighter than the white china, because these being better absorbers, emit also much greater light. If we take a polished metal ball and have a black spot on it by coating it with platinum black, then on heating the ball to about 1000°C and suddenly taking it out in a dark room, it will be found that the black spot is shining much more brilliantly than the polished surface. Again take the case of a coloured glass. We know that green glass looks green because it absorbs red light strongly and reflects the green (red and green being complementary colours). Hence when a piece of green glass is heated in a furnace and then taken out, it is found to glow with a red light. Similarly a piece of red glass is found to glow with green light. A more decisive example illustrating selective action is that of erbium oxide, didymium oxide, etc., which when heated emit certain bright bands in addition to the continuous spectrum. If now a solution of these oxides is made and continuous light is passed through it, the very same bands appear in absorption.

16. Application to Astrophysics.—Besides these applications Kirchhoff's law was in a sense responsible for the birth of two entirely new branches of science, *viz.*, Astrophysics (physics of the sun and the stars) and Spectroscopy. We shall recount here briefly how these developments grew out of Kirchhoff's law. Newton had shown in 1680 that the sunlight can be decomposed by means of a prism into the seven colours of the rainbow, but Fraunhofer who repeated the experiment in 1901 with better instruments, found to his surprise, that the spectrum was not continuous, but crossed by dark lines. Their number is at present known to be 20000, but Fraunhofer noticed about 500 of them, and denoted the more prominent bands by the letters of the alphabet :—A, B, C,...... Such a solar absorption spectrum is shown in Fig. 9 (C) together with a continuous prismatic (A) and continuous grating spectrum (B).

Fraunhofer never understood how these dark lines originated, neither did any of his contemporaries. But he realized their great importance, measured them and catalogued their wavelengths. He examined the light from stars, and showed that their spectra were also crossed by dark lines just as in the case of the sun. A typical stellar spectrum is shown in Fig. 9 (E).

In the meantime, however, other sources of light were examined by the spectroscope and some knowledge was obtained of their spectra. It was found that a glowing solid gives a continuous spectrum, but a flame tinged with NaCl gives a pair of intense yellow lines on a dark background. It was found that if an electric discharge was passed through a glass tube containing gas at low pressure, a large number of emission lines were obtained on a dark background. For hydrogen these are shown in Fig. 9(D).

But still the dark lines of Fraunhofer remained unexplained. Some physicists, notably Fizeau, observed that if the spectrum of the sun is examined side by side with the spectrum from a sodium flame, the yellow lines appear in the same place as the D-band of the Fraunhofer spectrum. Similar is the case with the hydrogen spectrum. In Fig. 9(C) and (D) we see the emission spectrum of hyrogen side by side with the Fraunhofer spectrum. It is clearly seen that some of the dark lines in the latter occur in the same place as the bright lines in the former.

The explanation given by Kichhoff not only completely solved the problem, but was far-reaching and extremely fruitful in its consequences. He supposed that the central body of the sun consists of a glowing mass which emits a continuous spectrum without black lines. But this light has to pass through a cooler atmosphere surrounding the central mass. In this atmosphere all the elements like Na, Cu............, etc. are present in the gaseous form in addition to ordinary gases like H_2, N_2, O_2, etc.

We have seen how the early workers studied the phenomenon of radiation with simple apparatus and had arrived at some very general laws. Every substance when heated emits radiation, *i.e.*, light. Every substance has again got the power of absorbing light. Kirchhoff arrived at the same law from thermodynamic reasoning (sec. 19) and applied it to explain the dark lines. Sodium can emit the D-lines when it is excited; hence when white light falls on it, it can absorb also the same light, and allows other light to pass through it unmolested. The gases in the outer cooler mantle round the sun therefore deprive the continuous spectrum from the central mass, of the lines they themselves can emit, and give rise to the black lines. The D-bands therefore prove that there is sodium in the sun's atmosphere. Similarly, the other dark lines testify to the presence of their respective elements in the atmosphere of the sun.

The correctness of Kirchhoff's explanation is seen further from flash spectrum results. We have supposed that the atmosphere of

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CONTINUOUS PRISMATIC

(A)

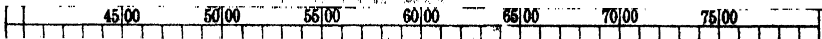
CONTINUOUS GRATING

(B)

SOLAR ABSORPTION GRATING

H G F E D C B a A

(C)

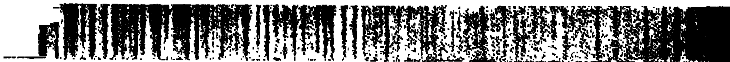


(D)

HYDROGEN BRIGHT LINE

SPECTRUM OF α-AURIGA (G_0 TYPE)

(E)



COMPARISON OF FLASH SPECTRUM
(1905) WITH ROWLAND ATLAS

(Flash photograph enlarged five times and Atlas reduced five times).

(F)

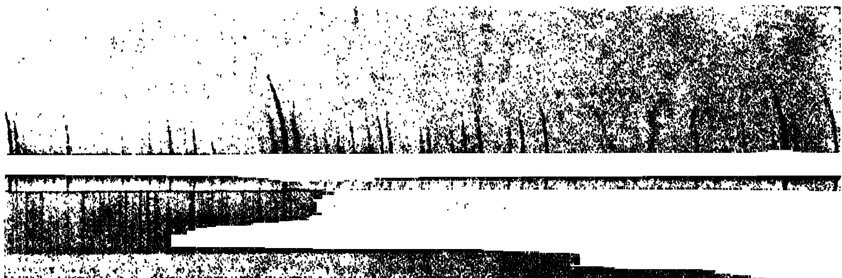


Fig. 9

Figs. (A), (B), (C), (D) have been reproduced from Knowlton, *Physics for College Students*, (E) from Muller-Pouillets, *Lehrbuch der Physik*, Vol. V, part 2, and (F) from *Handbuch der Astrophysik*, Vol. IV.

the sun contains Na. Now if we could observe the spectrum of the atmosphere apart from that of the central glowing core (the photosphere), the lines would appear bright. We cannot ordinarily do so because the solar atmosphere is so thin that we cannot cover up the disc properly, leaving the atmosphere bare oor our observation; further the scattered sky-light completely obscures the spectrum of the part outside the disc. But during a total solar eclipse, the solar disc is completely covered for a short time by the disc of the moon, and skylight is also reduced by the moon's shadow. To anyone observing the sun through a spectroscope, the solar atmosphere will be laid bare at the time of totality and the dark lines will flash out as bright lines. This was found actually to be the case by Young of Princeton in 1872. Fig. 9 (F) shows a flash spectrum of 1905 eclipse which is placed side by side with the Rowland Atlas of Fraunhofer spectrum for the sake of comparison. The lines of the flash spectrum are thus found to be due to the elements in the sun's atmosphere.

But Kirchhoff's discovery is of much more far-reaching importance than the mere success in explaining the Fraunhofer bands would indicate. It clearly asserted for the first time, *that every different type of atom, when it is properly excited, emits light of definite wavelength which is characteristic of the atom.* Just as a man is known by his voice, or a musical instrument by the quality of its note, so each atom can be recognised by the particular lines it emits. Thus was born the subject of Spectrum Analysis, which aims at identifying elements by their characteristic lines, and forty new elements were added with its aid to the list already known. The different atoms are regarded as so many different types of instruments, each capable of producing its own characteristic ætherial music.

APPLICATION OF THERMODYNAMICS TO RADIATION

17. Temperature Radiation.—Since material substances at all temperatures are found to emit radiation, it becomes possible to apply the laws of thermodynamics to the problems of temperature radiation. The expression "Temperature Radiation" should be clearly understood, for matter can be made to emit radiant energy in many ways other than by heating, *e.g.*, by passing an electrical discharge through it when in a gaseous state, by phosphorescene, fluorescence, or by chemical action as in flames. But Kirchhoff's law holds only for temperature radiation. For radiation produced by other methods the law cannot be applied.

18. Exchange of Energy between Radiation and Matter in a Hollow Enclosure.—Let us suppose that there is an enclosure with its walls, which are impervious to external radiation, maintained at a constant temperature. We shall study what takes place when we place substances having widely different physical properties within this enclosure.

In the first place the whole space is filled with radiation which is being emitted by the walls. This radiation arises out of the heat

energy of the walls, and should therefore be regarded as a part of this heat energy. If we now place a material body A inside the enclosure, it is easy to see that whatever the initial temperature of A might have been, *it will ultimately acquire the same temperature as the walls*.* This can be proved by the method of *reductio ad absurdum*, for suppose that in the equilibrium state the temperature is different. Then a Carnot engine may be used to transfer heat reversibly from the walls to A until A had the same temperature as the walls. During the process a certain amount of heat will be converted to work. But again A would be reduced automatically to a different temperature, as according to our assumption, this is the stable state of affairs. Hence again the difference of temperature can be utilized for the conversion of heat to work. We thus see that if the body were to assume a temperature different from that of the walls, we have at our disposal a means of continuously converting the heat of a single body to work without maintaining a second body at a lower temperature. This is against the second law and hence we conclude that all material bodies placed in the enclosure would ultimately assume the temperature of the walls.

Let us now suppose that a body of heterogeneous composition is placed within the enclosure. Then the different parts of the body have different emissive and absorptive powers. The total energy absorbed by the body will be equal to the energy it emits, since its temperature remains constant in the equilibrium state. Now the energy emitted by the body remains always the same from Prevost's law, whatever be the position or the orientation of the body with respect to the enclosure. It follows therefore that the total energy absorbed by the body remains the same even if its position or orientation with respect to the enclosure is changed. And as the different surfaces of the body have different coefficients of absorption, this can be the case only when the radiation travelling inside the enclosure in different directions is identical in quantity as well as quality (*i.e.*, isotropic).

We shall now prove that the radiation inside the hollow enclosure is *independent of the nature or the geometrical shape of the walls of the enclosure* or of any body placed inside it. Let us suppose that we have two enclosures A and B having walls of different shape and material and communicating with each other through a screen which allows radiation of wavelength lying between λ and $\lambda+d\lambda$ to pass through it. Now the walls of both A and B are maintained at the same temperature T. If in the steady state the intensity of radiation of the wavelength λ be greater in A than in B, some radiation will pass through the screen from A to B and the density of radiation will increase in B and decrease in A. The screen is then closed. The excess radiation will be absorbed by the walls of B and raise its temperature to T', while the temperature of the walls of A will fall.

* This may be easily seen for in the equilibrium state the entropy will be maximum and this can occur only when all temperature differences cease to exist.

Now a Carnot engine may be worked between these two temperatures yielding a certain amount of work and lowering thereby the temperature of B and increasing that of A till the two are brought to the same temperature. The process can be repeated and thus we can get an indefinite amount of work while the entire system (AB) will go on becoming colder. Thus in effect we are getting work indefinitely by using the heat of a single body. This is impossible by the second law of thermodynamics. Hence the intensity of radiation for every wavelength must be the same in the two enclosures, *i.e.*, the quality and intensity of radiation depends only upon the temperature and on nothing else.

If we now place a black body inside the enclosure, it will emit an energy of the same quality and intensity as it absorbs. Hence it follows that the radiation inside the enclosure is identical in every respect with the radiation emitted by a black body at the same temperature as the walls of the enclosure. These conclusions were arrived at by Kirchhoff in 1858.

19. Deduction of Kirchhoff's Law.—Suppose we have a uniformly heated enclosure containing some substance whose emissive and absorptive powers for radiation of wavelength lying between λ and $\lambda + d\lambda$ are e_λ and a_λ respectively. We have already shown in the previous section that the amount of radiation dQ falling on the substance from the walls does not depend upon the nature or the shape of the walls. Of this a portion $a_\lambda\, dQ$ is absorbed by the substance while the remainder $(1-a_\lambda)\, dQ$ is reflected or transmitted. Further the substance will emit radiation equal to $e_\lambda d\lambda$ by virtue of its temperature. Equating the energy absorbed to the energy emitted we have

$$e_\lambda d\lambda = a_\lambda dQ. \qquad \dots \qquad (5)$$

In the case of a perfectly black body of emissivity E_λ we have (since $a_\lambda = 1$),

$$E_\lambda d\lambda = dQ. \qquad \dots \qquad (6)$$

Combining (5) with (6) we get

$$\frac{e_\lambda}{a_\lambda} = E_\lambda. \qquad \dots \qquad (7)$$

i.e., at any temperature the ratio of the emissive power to the absorptive power of a substance is constant and equal to the emissive power of a perfectly black body. This is the thermodynamic proof of Kirchhoff's law. We have proved the law here for bodies inside the enclosure. Now since the emissive and absorptive powers depend only upon the physical nature of the body and not upon its surroundings, it follows that the law will hold for all bodies under all conditions for pure temperature radiations.

20. The Black Body.— The considerations put forward in sec. 18 enable us to design a perfectly black body for experimental purposes. We have seen that if an enclosure be maintained at a constant temperature it becomes filled with radiation characteristic of a perfectly black body. If we now make a small hole in the wall and examine the radiation coming out of it, this diffuse radiation will be identical with radiaton from a perfectly black emissive surface. The smaller the hole, the more completely black the emitted radiation is. Thus a correction has to be applied for the lack of blackness due to the finite size of the hole. This is due to the fact that some of the radiation coming from the wall is able to escape out and the state of thermodynamic equilibrium as postulated in section 18 does not hold. This is almost completely avoided in the particular type of black body due to Fery (Fig. 11, p. 297). So we see that the uniformly heated enclosure behaves as a black body as regards emission and if we make a small hole in it, the radiation coming out of it will be very nearly blackbody radiation.

Again such an enclosure behaves as a perfectly black body* towards incident radiation also. For any ray passing into the hole will be reflected internally within the enclosure and will be unable to escape outside. This may be further improved by blackening the inside. Hence the enclosure is a perfect absorber and behaves as a perfectly black body.

Though Kirchhoff had proved in 1858 that the radiation inside

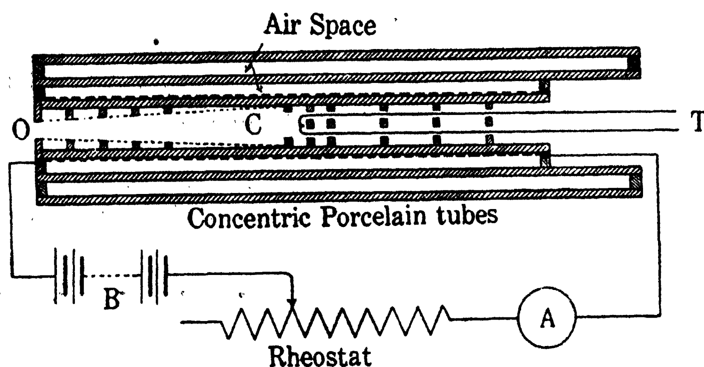


Fig. 10.—Black body of Wien.

a uniformly heated enclosure is perfectly black it was long afterwards in 1895 that Wien and Lummer utilised this conception to obtain a black body for experimental purposes.

The black body of Wien consists of a hollow cylindrical metallio chamber C (Fig. 10) blackened† inside and made of brass or platinum,

* Kirchhoff defines a black body as one "which has the property of allowing all incident rays to enter without reflection and not allowing them to leave again." See Planck, *Warmestrahlung.*

† The walls however need not be black. Blackening merely enables the equilibrium state to be reached quickly.

depending upon the temperature that it has to stand. The cylinder is heated by an electric current passing through thin platinum foil as indicated by thick dashes. The radiation then passes through a number of limiting diaphragms and emerges out of the hole O. The cylinder is surrounded by concentric porcelain tubes. The temperature of the black body is given by the thermo-element T. This is the type of black body now commonly used.

Another type due to Fery is shown in Fig. 11. Note the conical projection P opposite the hole O. This is to avoid direct radiation from the surface opposite the hole which would otherwise make the body not perfectly black.

A striking property of such an enclosure is that if we place any substance inside it, the radiation emitted from it is also black and independent of the nature of the body. Thus all bodies inside the enclosure lose their distinctive properties. For a mirror placed inside will reflect the black radiation from the wall and hence the emitted radiation is black. Any substance if it absorbs any radiation transmitted from behind must emit the same radiation in consequence of Kirchhoff's law and the total radiation leaving it must become identical with that from the walls *i.e.*, of a black body.

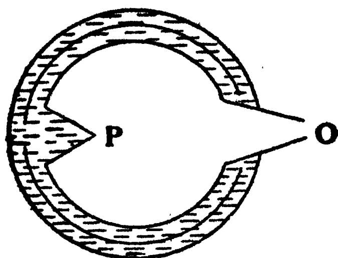


Fig. 11.—Black body of Fery.

RADIOMETERS

21. Sensitiveness of the Thermopile.—We shall now describe the instruments which are used for the measurement of radiation. The differential air thermometer, which was employed by Leslie and the early workers, has already been described in sec. 2, but is now only of historical interest.

Among the modern instruments, the thermopile has been described in sec. 2. Special care however has to be taken in order to make it sensitive as we have sometimes to measure very small amounts of energy. In the design of thermopiles, the following considerations have to be borne in mind:—(1) metals used should give large thermo-E.M.F.; (2) junctions should be as thin as possible; (3) connecting wires should be thin so as to minimise the loss of heat by conduction; (4) the junction should be coated with lampblack so that all the heat falling on it may be absorbed; (5) it should be mounted in vacuum, so that there is no loss of heat by convection, and the deflections remain steady; a rocksalt window is provided to let in the incident radiation.

The sensitiveness also depends upon the number of thermo-junctions but this cannot be increased indefinitely as the external

resistance will increase. The best procedure is to have the piles as light as possible and to choose a number so that the total resistance of the thermopile is equal to the galvanometer resistance.

The galvanometer to which the thermopile is connected should be of low resistance type with high voltage sensitiveness. For ordinary work the suspended coil type galvanometers are generally employed but are not sufficiently sensitive on account of their high resistance. For accurate work the suspended magnet (astatic) type of galvanometers are generally employed, namely, the Broca, the Paschen and the Thomson galvanometers. These are however very much susceptible to external magnetic disturbances and can be successfully used only by skilled workers.

The Linear Thermopile—The extreme sensitiveness of the galvanometers mentioned above enables us to work with only a few pairs of thermo-elements. The hot junctions are all arranged in a vertical line. The wires are very fine and are wound on a small frame. This is called the linear thermopile and is used for investigating the lines of the infra-red spectrum.

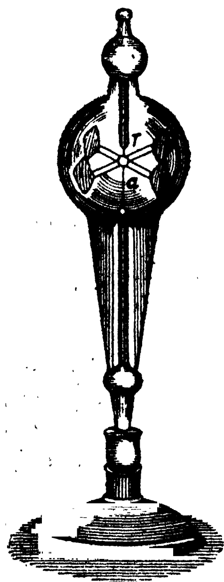


Fig. 12.—Crookes' radiometer.

22. Crookes' Radiometer—This consists of a number of thin vertical vanes of mica suspended at the ends of a light aluminium rod *r* inside an evacuated glass vessel (Fig. 12). Two such rods fixed at right angles are shown in the figure. They are suspended in such a way that they can rotate about the vertical axis *a*. The outer face of the vanes is coated with lampblack, while the inner faces are left clear. When radiation (thermal or light) falls on the blackened face the vanes begin to revolve in such a direction that the blackened face continually recedes away from the source of radiation.

The cause of this motion is easily understood. The blackened face absorbs the incident radiation and thereby its temperature is raised, while the clear face remains at a lower temperature. The molecules bombarding the blackened face therefore become more heated than the molecules bombarding the other side of the vane and consequently they exert greater pressure on the vanes. The result is that there is a net effective force repelling the vanes from the incident radiation. This is known as the *radiometer effect* and is essentially due to the presence of molecules. It is obvious that the velocity of revolution will be a measure of the intensity of radiation.

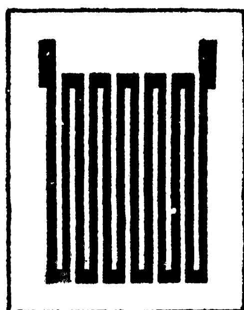
By suspending the vanes by means of a quartz fibre as in galvanometers we can measure the intensity of radiation if we observe

the steady deflection produced. Such a radiometer has been employed by some investigators for measuring the intensity of radiation.

23. The Bolometer.— The bolometer is now rather rarely used, being superseded by modern types of thermopile. It was invented by Langley and depends for its action on the change of resistance of platinum strips or wires when heated.

The sensitiveness of the bolometer depends (1) on the sensitiveness of the galvanometer; (2) on the thinness of the strips, because the thinner the strips the larger will be the rise in temperature and the increase in resistance for a given amount of incident radiation.

Two types of bolometers have been used in radiation measurements: (1) the surface bolometer for total radiation measurements,



Figs. 13 and 14.—The Surface Bolometer.

(2) linear bolometer for measurement of distribution of energy in the spectrum of a black body.

The surface bolometer consists of exceedingly thin strips of platinum, 1 to 2×10^{-3} mm. thick, joined together in series. The method of constructing such a thin conductor is as follows:—A sheet of platinum is welded to a thick sheet of silver and the composite sheet is rolled. The sheet is then punched out as shown in Fig. 13, and attached to a hollow frame of slate. The silver is then dissolved off in nitric acid, the end joints being protected by a coating of varnish. The strips are then coated with platinum black. Fig. 14, shows a front view of such a grid. A grid so constructed has a resistance of about 60 ohms.

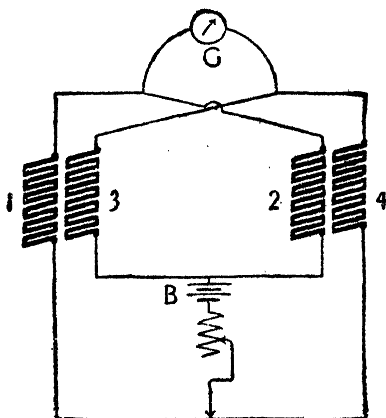


Fig. 15.—Connections of the Bolometer.

For experimental purposes four such grids, similar in all respects to each other are connected in the form of a Wheatstone

bridge. The method of connecting the grid is shown in Fig. 15. The grids 1 and 3 are in opposite arms of the Wheatstone bridge and are so arranged that the strips in 3 receive the radiation passing between the strips in 1 and so the effect is doubled. 2 and 4 are similarly arranged but are protected from radiation. The whole is enclosed in a box. In the absence of incident radiation the galvanometer shows no deflection. When radiation is incident on grids 1 and 3 deflection is produced.

In the linear bolometer a single narrow and thin strip of platinum is used.

24. The Radiomicrometer.— This was invented by Boys and is essentially a thermocouple without an external galvanometer. A single loop *c* of fine copper or silver wire is suspended (Fig. 16) between the poles of a strong permanent magnet NS as in a suspended coil galvanometer. To the lower ends of the copper wire two thin bars of antimony Sb and bismuth Bi are attached, and the lower ends of these are again attached to a thin disc *d* or narrow strip of blackened copper. To the upper end of the copper loop is attached a thin glass rod *g* carrying a light galvanometer mirror *m* for measuring deflection, the glass rod itself being attached to a fine quartz suspension *q*. The whole system is extremely light. Radiation, falling horizontally on the copper disc, heats the junction of antimony and bismuth and an electric current flows through the copper coil causing a deflection which depends upon the intensity of the energy received by the copper disc. To prevent disturbance due to diamagnetism of bismuth, the rods of the thermocouple are surrounded by a mass of soft iron. The whole suspended system is enclosed in brass (shown shaded in the diagram).

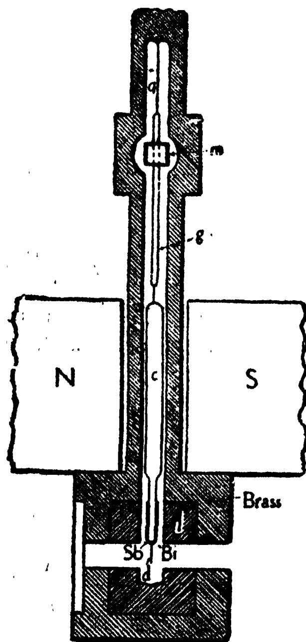


Fig. 16.*—Boys' Radiomicrometer.

25. Pressure of Radiation.— As radiation has been shown to be identical with light, it possesses all the properties which are ascribed to light. One of the properties of light most important for our present purpose is that it exerts a small but finite pressure on surfaces on which it is incident. This had been suspected by philosophers for a long time since the days of Kepler, who observed that as the comets approach

* Reproduced from "The Theory of Heat" by Preston by the kind permission of Messrs. Macmillan & Co.

the sun, the tail of the comet continuously veers round, so as to be always opposite the sun (Fig. 17). This he tried to explain on the assumption that light exerts pressure on all material bodies on which it is incident, but the pressure increases in importance only when the size of the particle is reduced. The rays of the sun heat cometary matter, either dust particles or atoms, which are then repelled by light-pressure and thus form the tail. Though painstaking experimental investigations failed to show the existence of pressure of light, Maxwell propounded in 1870 his Electromagnetic Theory of Light, and showed that even on this theory Light should exert a pressure but this is very small, being equal to the intensity divided by the velocity of light or to the energy-density. Calculation shows that the pressure due to sunlight is equal to $4{\cdot}5 \times 10^{-5}$ dynes per cm.^{2}

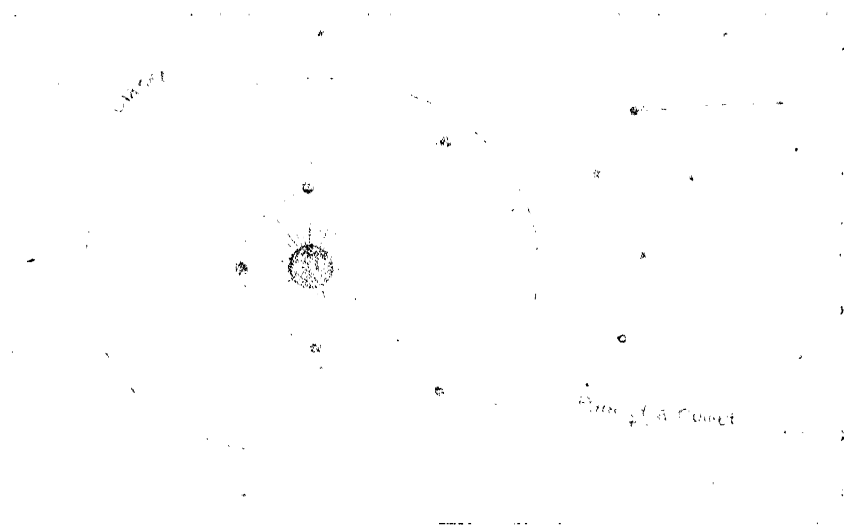


Fig. 17.—Tail of the comet.

Bartoli also showed from thermodynamic considerations that radiation should exert some finite pressure. The pressure of radiation is however so small that for a long time it baffled all attempts to measure it. The difficulties were overcome only in 1900 when Lebedew, and a little later, Nichols and Hull demonstrated experimentally its existence and were able to measure it. They confirmed the theoretical conclusion that pressure is equal to the energy density of radiation.

When the radiation is diffuse, it can be shown that pressure is equal to one-third the energy density of radiation.

The fact that radiation exerts a finite pressure, however small it may be, is of great importance in the theory of black-body radiation. It shows that black radiation is just like a gas, for it exerts pressure

and possesses energy. In fact we can regard the black radiation as a thermodynamic system and calculate its energy and entropy, and apply the thermodynamic laws and formulæ. We shall make use of these ideas in the next section.

26. Total Radiation from a Black Body.—The Stefan-Boltzmann Law.—As already mentioned in sec. 7, J. Stefan, in 1879, deduced empirically from the experimental data of Dulong and Petit that the total radiation from any heated body is proportional to the fourth power of its absolute temperature. In 1884 Boltzmann gave a theoretical proof of the law based on thermodynamical considerations. He showed that the law applies strictly to emission from a black body. The law is therefore generally known as the Stefan-Boltzmann law, and may be formally enunciated as follows: —*If a black body at absolute temperature T be surrounded by another black body at absolute temperature T_0 the amount of energy E lost per second per square centimetre of the former is*

$$E = \sigma(T^4 - T_0^4), \qquad (8)$$

where σ is called the Stefan's constant.

For proving this law, we consider radiation in a black-body chamber and apply the thermodynamical laws to the radiation as mentioned in the previous section. Let u denote the energy density of radiation inside the enclosure, V its volume and p the pressure of radiation. Then both u and p are simply functions of the absolute temperature T. We have further the total energy U of radiation equal to uV. Applying* equation (61) p. 267 we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\partial p}{\partial T} - p \qquad (9)$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = u, \ p = \frac{u}{3}, \qquad (10)$$

since the radiation is diffuse (sec. 25). Hence equation (9) reduces to

$$u = \frac{T}{3}\frac{\partial u}{\partial T} - \frac{u}{3},$$

or

$$\frac{du}{u} = 4\frac{dT}{T},$$

or

$$u = aT^4, \qquad (11)$$

where a is a constant, independent of the properties of the body. Hence the total energy lost on one side by emission will also be proportional to the fourth power of the absolute temperature. That is the Stefan-Boltzmann law.

27. Experimental Verification of Stefan's Law.— The law was subjected to experimental test by various investigators. Lummer and

* Boltzmann deduced the law by imagining the radiation to perform a Carnot cycle. He utilized the conceptions of Bartoli. This is however unnecessary here for we have shown black radiation to be analogous to a gas and can therefore proceed directly to apply the general thermodynamical laws to radiation.

Pringsheim investigated the emission from a black body over the range of temperatures 100°C to 1260°C and found the law to hold true within experimental errors. We give below a brief account of their apparatus and arrangement.

A is a hollow vessel containing boiling water (Fig. 18) which acts as a standard source of radiation for calibrating the bolometer from time to time. The black body C employed for the range of temperatures 200°C to 600°C consisted of a hollow copper sphere blackened inside with platinum-black, and placed in a bath of a mixture of sodium and potassium nitrates which melts at 219°C. This salt bath could be maintained at any desired temperature. The temperature could be measured with a thermo-element T.

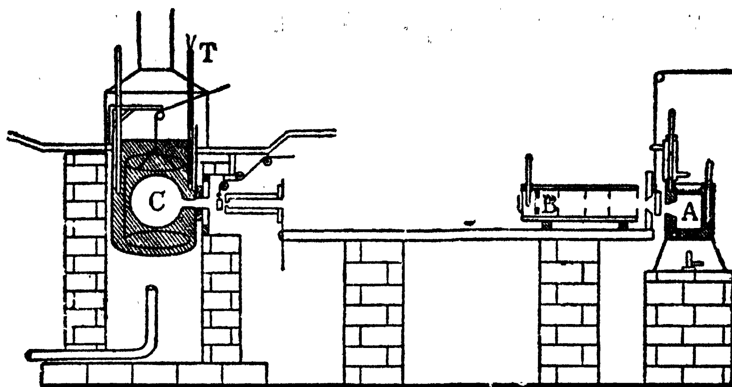


Fig. 18.—Lummer and Pringsheim's apparatus for verifying Stefan's law.

For temperatures between 900°C and 1300°C the black body shown in Fig. 19 was employed. D is an iron cylinder coated inside with platinum-black and enclosed in a double-walled gas furnace. The temperature inside the iron cylinder was obtained by a thermo-element enclosed in a porcelain tube passing through the furnace.

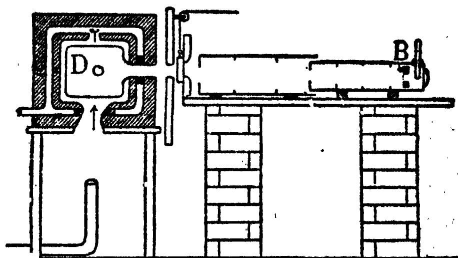


Fig. 19.—Black body for 900° to 1300°C.

The measuring instrument shown at B was the surface bolometer of Lummer and Kurlbaum. A description of this as well as the method of connecting it has been already given in sec. 23. Besides there are a number of water-cooled shutters so that the radiation can be stopped or allowed to fall at will.

The procedure adopted was as follows :—The bath was heated up to the desired temperature and maintained steady, and then the

shutter was raised to allow radiation from C to fall on the bolometer, and the maximum deflection registered by the galvanometer noted. The bolometer was kept at different distances from the black body and the inverse square law verified. Next observations were taken with the black body at different temperatures. The observations were all reduced to a common arbitrary unit depending on the radiation from the black body A at 100°C, and kept at a distance of 633 mm. If d represents the deflection of the galvanometer needle, T the absolute temperature of the black body, 290° the temperature of the shutter protecting the bolometer, then

$$d = a(T^4 - 290^4), \quad . \quad . \quad . \quad (12)$$

from Stefan's law. The coefficient a was found to be constant. Hence the truth of Stefan's law is established.

DISTRIBUTION OF ENERGY IN THE SPECTRUM OF A BLACK BODY

28. Laws of Distribution of Energy in Blackbody Spectrum.— From a study of the colour assumed by bodies when their temperature is gradually raised (see p. 281) it will be obvious that as the temperature of a body is raised, the colour emitted by it becomes richer in waves of shorter wavelength. In fact the wavelength for which the intensity of emission is maximum shifts towards the shorter wavelength side as the temperature is raised. These results were also arrived at by Wien in 1893 from thermodynamic considerations of black radiation inside a hollow reflecting chamber. He showed that $E_\lambda \, d\lambda$ the amount of energy contained in the spectral region included within the wave lengths λ and $\lambda + d\lambda$ emitted by a black body at temperature T is of the form

$$E_\lambda \, d\lambda = \frac{A}{\lambda^5} f(\lambda T) d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and further if λ_m denotes the wavelength corresponding to the maximum emission of energy and E_m the maximum energy emitted,

$$\lambda_m T = b, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$E_m T^{-5} = B, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where B and b are constants. In other words, if the temperature of radiation is altered, the wavelength of maximum emission is altered in an inverse ratio. Equation (13) is known as *Wien's Displacement law.*

A further step forward in developing the theory was taken by Planck who showed from very novel considerations (which developed into the modern quantum theory) that the energy density of radiation inside the enclosure is given by

$$u_\lambda d\lambda = \frac{C_1}{e^{c_2/\lambda T} - 1} d\lambda, \quad . \quad . \quad . \quad . \quad (16)$$

where $C_1 = 8\pi hc/\lambda^5$ and $c_2 = ch/k = 4{\cdot}96\, b$ approximately. This is

known as *Planck's law*. We shall now consider how the spectra can be obtained experimentally and the foregoing results verified.

29. Experimental Study of the Black-body Spectrum.— The first systematic study of the infra-red spectrum was undertaken by Langley who illuminated the slit of a spectrometer by means of sunlight and produced the spectrum by a prism of rocksalt. The rays were focussed by a lens on a bolometer which was arranged in a Wheatstone bridge adjusted for no deflection.

The spectrum can also be produced by a Rowland grating but on account of the considerable overlapping of spectra of different orders prisms have been generally employed. Lenses of quartz or fluorite are generally used. It is however better to use a concave mirror for focussing the radiation.

Wien's displacement law was subjected to a series of experimental tests by Paschen, Lummer and Pringsheim, Rubens and Kurlbaum. We give below a short description of the experiment and results of Lummer and Pringsheim (1899). They used radiation from an electrically heated carbon tube and produced the spectrum by refraction through a fluorspar prism. The distribution of energy was measured by means of a linear bolometer which was enclosed in an air-tight case to diminish the absorption due to water vapour and carbon dioxide. Corrections were applied to convert the prismatic spectrum into a normal one by means of the known dispersion curve of fluorspar. The distribution of energy in the spectrum for various temperatures between 621°K and 1646°K was obtained and curves plotted (Fig. 20). The ordinates represent emissive powers and the abscissæ wavelengths. The full

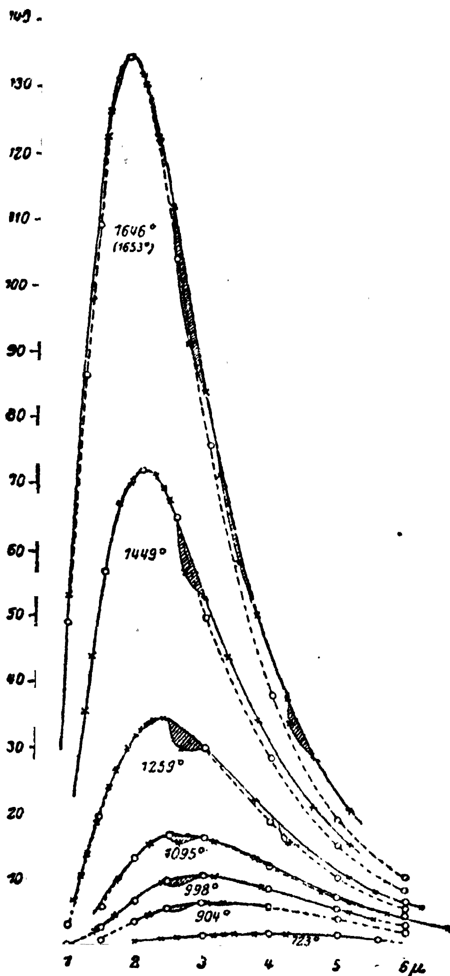


Fig. 20.—Distribution of energy in the blackbody spectrum.

lines denote the curves obtained experimentally while the dotted lines represent the curves calculated from a semi-empirical law given by Wien. The total radiation at a temperature is represented by the area enclosed between the curve and the x-axis and varies as T^4. The small patches of shaded area represent the absorption bands of carbon dioxide and water vapour. The absorption of fluorspar begins at 6μ where the curves are seen to end abruptly. The wavelength of maximum emission shifts towards the origin as the temperature rises. From these curves the values of E_m and λ_m could be read. The experimental data are given in Table I.

Table 1.—Experimental Verification of Wien's Displacement Law.

Temp. °K	λ_m in μ's	E_m	$\lambda_m T$ in micron degrees	$E_m T^{-5} \times 10^{17}$
1646	1·78	270·6	2928	2246
1460·4	2·04	145·0	2979	2184
1259·0	2·35	68·8	2959	2176
1094·5	2·71	34·0	2966	2164
998·5	2·96	21·5	2956	2166
908·5	3·28	13·36	2980	2208
723·0	4·08	4·28	2950	2166
621·2	4·53	2·026	2814	2190
		mean =	2940	2188

The table shows clearly the validity of equations (14) and (15). Knowing the value of b or B these laws enable us to determine the temperature of any substance (assumed to be a black body) if λ_m or E_m be found out. The value of b is seen to be ·294 cm × degree and of B to be $2{\cdot}188 \times 10^{-14}$ ergs × degree.

This furnishes us with a simple method of determining the temperature of the heavenly bodies. Thus for the moon $\lambda_m = 14\mu$ and hence

$$T = \frac{\cdot 294}{14 \times 10^{-4}} = 210^\circ \text{K}.$$

Similarly we can calculate the temperature of the sun (sec. 42).

PYROMETRY

30. Gas Pyrometers.— In Chapter 1 we have already described the constant volume hydrogen thermometer having a platinum-iridium bulb. For temperature above 500°C hydrogen cannot be used as the thermometric gas because the platinum bulb is permeable to it; hence nitrogen is invariably employed. As regards the material of the bulb Jena glass can be used to about 500°C while quartz glass can stand up to about 1300°C but is attacked by traces of alkali from

hand etc. Ordinary porcelain is porous and permeable to the thermometric gas but glazed porcelain was formerly employed up to about 1000°C above which however the glazing softens and breaks; also its expansion is not regular. Platinum alloys are now invariably used. An alloy of platinum and iridium was employed by Holborn and Valentiner up to 1600°C. Iridium however distils and also makes the bulb brittle. Holborn and Day found the alloy of 80Pt-20Rh best for the purpose and used a modified form of bulb of this material to about 1600°C. They performed experiments with great care and took into account 25 possible sources of error so that their values are regarded as standard at high temperatures. The correction however becomes enormous at these high temperatures and hence there is considerable uncertainty in determining the high temperature fixed points with a gas thermometer.

31. Resistance Pyrometers.— The platinum resistance pyrometer has been described in Chapter 1. It can be used to about 1200°C though the melting point of platinum is 1770°. If used above 1000°, however, the platinum undergoes some change and does not return to its initial zero and has to be restandardised. The mica insulation also sometimes breaks due to moisture getting inside.

32. Thermo-electric Pyrometers.— The thermo-electric pyrometers have been completely described in Chapter 1. It is shown there that for temperatures up to 600°C the base couples Cu-constantan, nickel-silver are the most sensitive. The Pt, 90Pt-10Rh couple is however best for all high temperature work and can be used to about 1750°. It is free from parasitic disturbances and changes in composition, and is the most sensitive pyrometer in the range 1000° to 1600°. In the lower range however it can be replaced by Ni, 90Ni-10Cr couple up to 1300°C when the latter is much more sensitive. A couple of Ir, 90Ir-10Ru can be used to about 2100°C while thermocouples of tungsten and an alloy of tungsten with molybdenum have been used up to 3000°C.

RADIATION PYROMETER

33. Temperature from Radiation Measurements.— In the foregoing pages we have seen that the radiation emitted by a black body depends upon its temperature and upon nothing else. Hence if we measure the radiation emitted by the body with the help of some instrument we can find its temperature. We may either measure the total radiation emitted by the body and deduce the temperature by making use of Stefan's law (equation 8). These are called 'Total Radiation Pyrometers.' Or we may measure the energy $E_\lambda \, d\lambda$ emitted in a particular portion of the spectrum and make use of Planck's law (equation 16) of distribution of energy in the spectrum. These are called Spectral or Optical pyrometers.

Radiation pyrometers possess the great advantage that they can be employed to measure any temperature, however high that may be or wherever the object may be. The pyrometer itself has not to

be raised to that temperature nor need it be placed in contact with the hot body. Further there is no extrapolation difficulty as the radiation formulæ have been found to hold rigorously for all temperatures. But the radiation pyrometer suffers from a serious drawback. It can measure accurately the temperature of black bodies only.

It is, however, generally employed to measure the temperature of any hot source. In that case it gives that temperature at which a perfectly black body would have the same intensity of emission (total or spectral) as the body whose temperature is being measured. This temperature is called the *blackbody temperature* of the substance and is consequently lower in all cases than its actual temperature. The greater the departure from perfect blackness the greater is the error involved. The lower practical limit for radiation pyrometers is about 600°C, for then the emission from substances becomes too small to be measured accurately. Still, however, with certain devices it can be used to measure much lower temperatures as that of the moon.

34. Total Radiation Pyrometers.— Fery was the first to devise a radiation pyrometer based on Stefan's law. These pyrometers are merely thermopiles so arranged that the readings are independent of the distance between the hot body and the pyrometer. We shall describe Fery mirror pyrometer which is typical of this class. Fig. 21 shows a modern type of instrument. Radiation incident from the right side falls on the concave mirror M which can be moved backwards and forwards for the purpose of focussing the radiation on the receiver S to which the hot junction of the thermocouple is attached. The cold junction of the thermocouple is protected from radiation by the tongue T and is further surrounded by the box B which also contains the thermocouple receiver, and a small opening just in front of S. The electromotive force developed is read on a millivoltmeter connected as indicated in Fig. 21. The instrument possesses no lag, the steady state being reached in about a minute. To enable the observer to focus the radiation accurately on the thermocouple, Fery employed two semi-circular mirrors, inclined to each other at an angle of about 5° and placed immediately in front of S, an opening of about 1·5 mm. being left at the centre of the mirror to allow the incident radiation to pass. Now if the image of a straight line formed by the concave mirror does not lie in the plane of the inclined mirrors they will form two images separated by a distance (see Fig. 22) and the line will

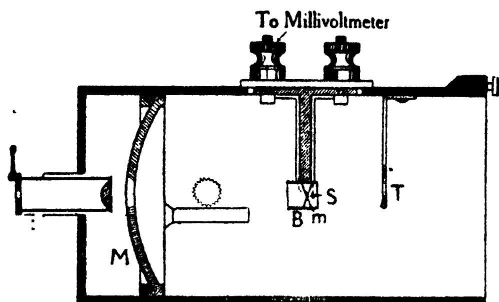


Fig. 21.—Fery radiation pyrometer.

appear broken when seen through the eyepiece. The concave mirror is moved till this relative displacement of the two halves of the image disappears, and then the apparatus becomes adjusted. It will be easily seen that so long as the heat image formed by the concave mirror is larger than the hole, the thermocouple measures the intensity of the heat image and not the total radiation. For if the distance of the object is doubled, the amount of radiation falling on the mirror

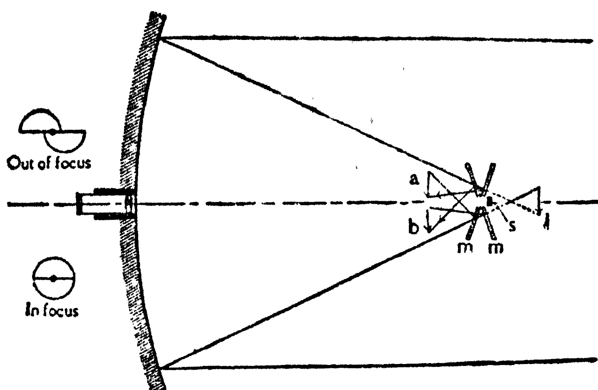


Fig. 22.—The focussing device.

is reduced to one-fourth, but as the area of the image is also simultaneously reduced to one-fourth the intensity is unaltered. Thus the indications of the instrument are independent of the distance. Hence in actual use it is essential that the object, whose temperature is to be measured, should be sufficiently large and should be placed at not very great distance in order that its image is always bigger than the aperture in the box which in ordinary instruments is about 1·5 mm. in diameter.

The E.M.F. of the couple in these cases is given by the relation

$$V = a(T^b - T_0{}^b), \qquad . \quad . \quad . \quad (17)$$

where T is the temperature of the black body to be measured, T_0 the temperature of the receiver S and b a constant which varies from 3·8 to 4·2 depending upon the instrument. Generally T_0 can be neglected in comparison with T. This departure from the index value of 4 is due to various causes. It is for this reason that the pyrometer has to be calibrated by actual comparison with a standard thermometer using radiation from a blackbody chamber or heated strip.

35. Optical pyrometers.— In these, the intensity of radiation from a blck body in a small width of the spectrum lying between λ and $\lambda + d\lambda$ is compared with the intensity of emission of the same colour from a standard lamp. The formulæ required for this case can be easily worked out by assuming Planck's law. There are two types of optical pyrometers :—(1) the Disappearing Filament type, (2) the Polarising type. We now proceed to describe these instruments.

36. The Disappearing Filament Type.— This type of pyrometer was first introduced by Morse in America. It was later improved by Holborn and Kurlbaum, and by Mendenhall and Forsythe. A pyrometer of this type is shown in Fig. 23 and is essentially a telescope having a lamp at the position usually occupied by the cross-wires. C is a metal tube containing the filament of a lamp L which is heated by the battery B and the current can be adjusted to any amount by varying the rheostat R. Radiation from the source whose temperature is required is focussed by the lens D on the lamp L where a heat image is formed. The lamp is viewed through the eyepiece E in front of which is placed a red filter glass. Besides there are a number of limiting diaphragms. In making an experiment the observer looks through E and varies the current in the lamp till the filament becomes invisible against the image of the source. If the current is too strong the filament stands out brightly while if the current is too weak, the filament looks black. The filter glass enables this matching to be done for approximately monochromatic radiation. The instrument is calibrated by direct comparison with a standard thermocouple and then extrapolated by the use of rotating sectors. Thus from the strength of the current required to match the radiation the temperature of the incident radiation can be deduced. Sometimes the ammeter is directly calibrated in degrees.

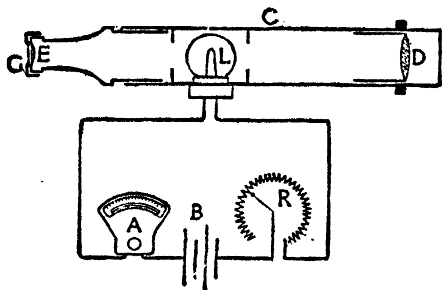


Fig. 23.—Disappearing Filament Pyrometer.

37. Polarising Type.— In 1901 Wanner constructed another pyrometer in which the comparison was made by the aid of a polarising device. Here the ray of a particular colour obtained from the source is compared with a ray of the same colour obtained from a standard

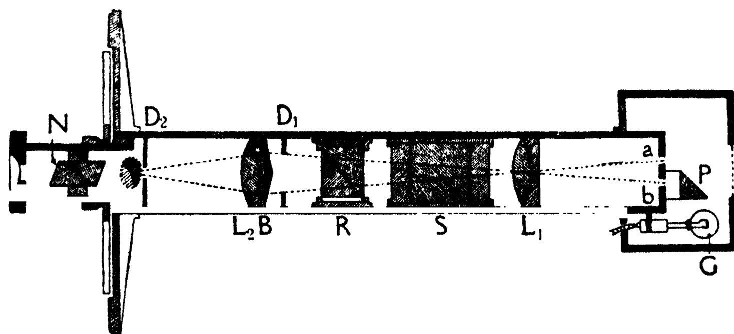


Fig. 24.—The Wanner Pyrometer.

electric lamp. A diagram illustrating the essential parts of the instrument is given in Fig. 24. a, b are two circular holes arranged symmetrically about the optical axis of the system. Radiation from the hot source enters the system through a, while the comparison beam is supplied by the electric lamp G which illuminates the right-angled prism P and the latter directs the light on to b. Both beams are rendered parallel by means of an achromatic lens L_1, which is placed at a distance from the slit equal to its focal length. The parallel beams are dispersed by the direct vision spectroscope S and then pass through the polarising Rochon prism R which separates each beam into two beams polarised in orthogonal planes. B is a biprism placed in contact with a second achromatic lens L_2 which focusses the two beams on the slit D_2. The biprism produces in the two beams deviations of such amount that one image from each source is brought into juxtaposition. Since the holes a, b are at the focus of the lens L_1 the images produced by the second lens are also circular but the biprism splits them into semicircles. Six out of the eight images are stopped out while the remaining two are observed through the nicol N.

If the two beams are of equal intensity a uniformly illuminated disc with a diametrical line is observed if the plane of polarisation of the nicol prism makes an angle of 45° with the plane of polarisation of each component. Rotating the nicol in either direction diminishes the brightness of one image and augments that of the other. If the two beams are of unequal intensity matching is affected by rotating the nicol prism in either direction. A graduated circle is attached to the analyser to observe the angle of rotation.

Let the angle at which radiation from any source matches the lamp be ϕ. Then it can be shown that

$$ln \tan \phi = a + \frac{b}{T} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where T is the absolute temperature and a, b are constants. If we determine two values of ϕ corresponding to two values of T, we get a straight line from which the temperature for any value of ϕ can be read. In practice, the pyrometer is calibrated by a direct comparison with a stanard thermometer, and the disc is directly graduated in degrees.

RADIATION FROM THE SUN

38. The Solar Constant.— The sun emits radiant energy continuously in space of which an insignificant part reaches the earth. But even of this incoming radiation, a considerable portion is lost by reflection and scattering by the terrestrial atmosphere and is sent back to the interstellar space. The best reflecting constituents of the atmosphere are water, snow and cloud. The scattering is partly due to the dust particles and partly due to the air molecules and is generally small. Further the radiation is heavily absorbed by the earth's atmosphere, the total absorption varying from 20 to 40% depending

upon the time of the day and the season of the year, and the different parts of the spectrum are absorbed to a different degree. We naturally seek for a more constant quantity which is furnished by the rate at which solar radiations are received by one sq. cm. of black surface held at right angles to the sun's rays and placed at the mean distance of the earth provided there were no absorption in the atmosphere or provided the atmosphere were not present. This is called the *solar constant* and is generally expressed in calories per minute. We shall now give a method of determining the solar constant.

39. Determination of Solar Constant.—The Absolute Pyrheliometer.— Among the early workers who attempted to measure the solar constant were Pouillet, Langley and Wilson. The instruments with which the solar radiations are measured are called pyrheliometers. We shall describe the *water-stir pyrheliometer* employed in the Astro-

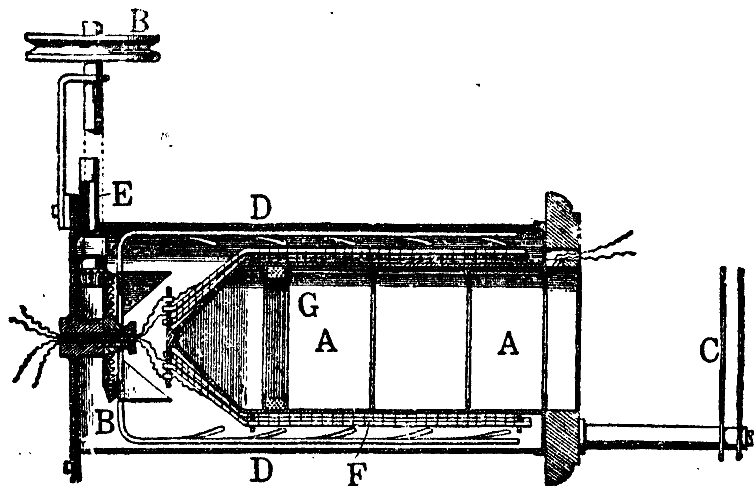


Fig. 25.—The water-stir Pyrheliometer.

physical Observatory of the Smithsonian Institution, Washington, U.S.A. Fig. 25 gives a cross-sectional view of the apparatus. AA is the black-body chamber for the reception of solar radiation, which is further protected from air currents by a vestibule, not shown. This is simply a hollow cylinder placed in front of AA. The chamber is blackened inside and has its rear end of conical shape, and is surrounded by water contained in the calorimeter DD which is stirred vigorously by means of a stirring arrangement BB run by an electric motor from outside. C is a diaphragm of known aperture for admitting the solar radiation. The incident radiation is completely absorbed by the chamber producing a rise in temperature of the water contained in the calorimeter. This rise is measured by the platinum resistance thermometer F whose wire is carefully wound upon an insulating frame round AA. At E is inserted a mercury thermometer. The

calorimeter DD is carefully insulated from thermal effects occurring outside.

For calibrating the instrument, a known amount of electrical energy is supplied to the manganin resistance wire G and the rise in temperature noted. Thus the heat obtained by solar radiation can be compared with the heat generated electrically.

Another type of pyrheliometer is called the *water-flow pyrheliometer*. In these a steady stream of water flows past the absorption chamber and the temperature difference between the incoming and outgoing water is observed.

The above instruments are called absolute pyrheliometers since they measure the energy directly. For most purposes it is more convenient to employ secondary pyrheliometers in which radiation is absorbed by a blackened silver disc. They are previously calibrated by comparison with an absolute pyrheliometer.

With the help of these instruments we are able to measure the radiation received per minute at the earth's surface and from this we must calculate the solar constant. The radiation received varies with the time of the day, depending upon the zenith distance of the sun. If we assume the absorption to be due to an atmosphere of homogeneous composition, then applying Biot's law, we have

$$I = I_0 \, e^{-k_1 d}, \quad . \quad . \quad . \quad . \quad (19)$$

where d is the thickness of the medium traversed, I_0, I the intensity of the beam just at the beginning and the end of the medium. This holds strictly for a monochromatic ray and a homogeneous medium. In the atmosphere there is no homogeneity in dust content or in density in a vertical direction. In the actual experiment the intensity of solar radiation as received on the earth is observed for different elevations of the sun on the same day with constant sky conditions. Then d varies as sec z where z is the sun's zenith distance. Further assuming as a first approximation* that k_1 is the same for all wavelengths we can write

$$S = S_0 \, a^{\sec z}, \quad . \quad . \quad . \quad . \quad (20)$$

where S_0, S represent the true and the observed solar constant respectively, and a is called the *transmission coefficient* and varies from 0·55 to 0·85. Then taking logarithms

$$\log S = \log S_0 + \sec z \log a. \quad . \quad . \quad . \quad (21)$$

Plotting the values of log S as ordinates and the corresponding values of sec z as abscissæ we obtain a straight line whose intercept on the ordinate axis gives log S_0, whence S_0 is found.

* For accurate work k_1 or a is not assumed constant. Extrapolation is done for each wavelength separately and from this extrapolated curve the value of S_0 is found.

Accurate experiments give the mean value of the constant to be 1·937 calories per minute per sq. cm. The constant is found to fluctuate with the eleven-year cycle of the sun.

40. Temperature of the Sun.— The sun consists of a central hot core terminating in a surface called the photosphere. By the expression 'temperature of the sun' we generally mean the temperature of the photosphere. The temperature inside the central core is, however, much greater than this. We shall now describe some simple methods for determining the temperature of the photosphere of the sun, based on measurement of radiation.

41. Temperature from Total Radiation.—According to careful observations by Abbot and others the solar constant is 1·937 cal. per minute per cm². We can now find out what would be the temperature of a black surface free from any atmosphere and having dimensions and position of the sun which would emit the same total radiation at the distance of the earth. This naturally gives us the minimum value for the temperature of the photosphere.

Let the radius of the sun be r, then the amount of heat lost by the sun per second is

$$H = 4\pi r^2 \sigma T^4,$$

where T is the blackbody temperature of the sun. If we now describe a sphere of radius R concentric with the sun (R being the distance of the earth), then the energy will be spread over the surface $4\pi R^2$, and hence the amount received per unit surface of the earth is

$$S = \frac{4\pi r^2}{4\pi R^2}\sigma T^4,$$

or

$$T^4 = \left(\frac{R}{r}\right)^2 \frac{S}{\sigma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now r/R, the mean angular radius of the sun $= 959'' = 4{\cdot}649 \times 10^{-3}$ radians ; $\sigma = 5{\cdot}77 \times 10^{-5}$ ergs sec.$^{-1}$ cm.$^{-2}$ degree^{-4} ; $S = 1{\cdot}937$ cal. cm.$^{-2}$ min.$^{-1}$. Hence we obtain after substituting these values in (22) that $T = 5732°$K.

42. Temperature from Wavelength of Maximum Emission.— Wien's displacement law $\lambda_m T = 0{\cdot}2884$ cm. × degree (equation 14) may also be employed to determine the temperature of the sun. Abbot's investigations show that $\lambda_m = 4753$ A. U., whence $T = 6059°$K. This temperature is about 300° higher than the temperature deduced from total radiation. This divergence is easily understood if we remember the fact that contrary to the assumption made here, the sun does not actually radiate like a black body.

43. Temperature of Stars.— The stars are so many suns, only they are at enormous distances compared to the sun. The determination of their temperature is subject to the same uncertainties as in the

case of the sun, and the methods followed are almost identical except that here the total radiation method fails as it is often not possible to determine the diameter of stars. The temperatures are deduced from the distribution of intensity in their emission spectra by the application of equation (14), but the actual methods are far more complicated. The temperature of stars measured in this and other ways varies from 2500°C (red stars) to nearly 30,000°C (for bluish white stars).

Books Recommended.

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. 4, Article by Coblentz.

2. Planck, *Wärmestrahlung* or English translation by Masius.

3. E. Griffiths, *Methods of Measuring Temperature.*

4. Burgess, and Le Chatelier, *The Measurement of High Temperature.*

5. Abbot, *The Sun.*

CHAPTER XII

THERMODYNAMICS OF THE ATMOSPHERE

1. In the present chapter we shall consider the application of the principles already developed in this book to the earth's atmosphere. Before doing so, however, we shall first state some of the results already known to us from the study of the atmosphere.

DISTRIBUTION OF TEMPERATURE

2. Vertical Distribution of Temperature.— The results of aerological observations show that the temperature of the atmosphere decreases continuously as we go up in the atmosphere. By combining several observations made over a given region, the form of the curve

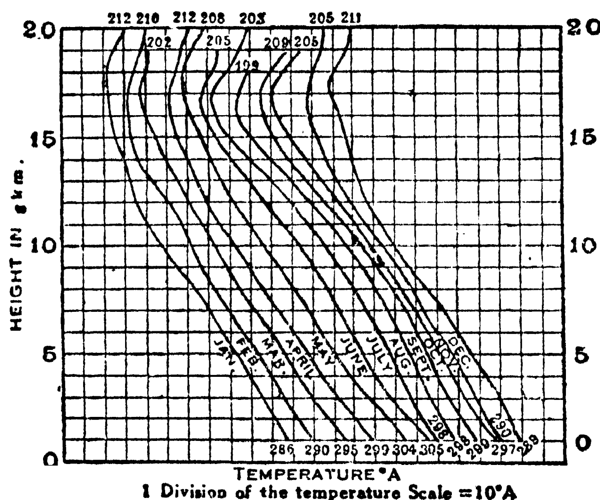


Fig. 1.—Vertical distribution of monthly mean temperatures over Agra.

giving the variation of temperature with altitude is determined. This curve varies slightly with the season, particularly at the lower levels. Fig. 1 gives the vertical distribution of the monthly mean temperature over Agra (lat. 17° 10′ N, long. 78° 5′E) in the Uttar Pradesh of India.

The fall of temperature due to a rise of 100 metres is usually called the vertical gradient of temperature and the fall of temperature per kilometre rise in altitude is usually known as the *lapse-rate* of temperature. The lapse-rate over any particular region varies with altitude and there is also a seasonal variation.

3. Troposphere and Stratosphere.— From Fig. 1 it is evident that over Agra up to a height of 13 to 16 km. there is a rapid fall of temperature, above which, however, the rate of fall diminishes and at a height of about 20 km. the temperature becomes almost constant,

i.e., the lapse-rate vanishes. A similar discontinuity in the vertical distribution of temperature in the atmosphere is noticed all over the world, although the height at which it occurs is not the same everywhere. The outer shell of the atmosphere, in which the temperature remains practically constant with variation of height, is given the special name of *Stratosphere* or *Advective Zone or Isothermal layer* to distinguish it from the *Troposphere* or the *Convective Zone*, which is the lower portion in which there is a considerable fall of temperature with height. The surface of separation of these two regions of the atmosphere, which plays a very important rôle in modern theories of atmospheric circulation, is called the *tropopause*. The height of the tropopause varies with the latitude. The tropopause seems to lower towards the ground as we proceed from the equator to the poles, its height being about 14 km. at the quator and about 8 to 10 km. at the poles and is greater in summer than in winter.

The causes of the diminution of temperature with height in the troposphere are manifold. Let us try to explain here in general terms why this temperature diminution occurs. The solar radiation* during its passage through the earth's atmosphere is only slightly absorbed by it, and the amount absorbed is distributed over such a large mass of air that the latter is not at all appreciably heated by the incident radiation. In contrast to this, however, the energy received by the earth is concentrated and therefore heats its surface considerably. The heated surface in turn warms the air above it, partly by contact and partly by the long wavelength radiated by it and absorbed by the air. Now the temperature of air at any height depends upon the total energy absorbed and emitted by it. The lower atmosphere at ordinary temperatures emits more energy than it absorbs and therefore tends to cool by radiation. These two phenomena, the heating of the earth and the cooling of the laver above, so affect the density of the atmosphere as to cause vertical convection, in consequence of which the warm ascending air becomes cooled through adiabatic expansion and the descending air becomes heated by adiabatic compression since the pressure of the atmosphere decreases with elevation. In this way the decrease of temperature with increase of elevation is established and maintained throughout the region in which vertical convection takes place. We shall calculate in §5 an expression for the lapse-rate.

Above a certain height, however, convection becomes feeble and the temperature of the atmosphere falls so much that the heat radiated by it becomes equal to the amount absorbed by it either directly from the earth's radiation or from the passing solar radiation. (This is because the heat radiation received by the air from the earth remains pactically constant at all available altitudes). The temperature of the layer remains practically unaltered at and above this height and therefore the convection currents cease above this height. The stratosphere therefore is a result of the cessation of convection currents and of establishment of radiative equilibrium.

* This has already been discussed on pp. 311-313.

4. Vertical Distribution of Pressure.— The theory of the diminution of pressure with increase of altitude is based on the application of the ideal gas laws to the atmosphere. Let us assume that the troposphere is in convective or adiabatic equilibrium while the stratosphere is in isothermal or radiative equilibrium. On account of convection currents the composition of the air in the troposphere is practically the same at all heights so that for the theoretical calculation of pressure we can assume a mean gas constant for the atmospheric air. For the stratosphere, however, convection currents cannot be assumed to exist since we have assumed the layer to be isothermal, hence no fixed value can be assumed for the gas constant R/M. We must therefore treat each constituent separately with its proper gas constant.

Let $-dp$ be the decrease of pressure corresponding to an increase of elevation dz. Then if ρ is the density of air at the point under consideration we have, on equating the decrease of pressure to the weight of the column dz,

$$-dp = g\rho dz. \quad . \quad . \quad . \quad . \quad (1)$$

From Boyle's and Charles' law we have $p = \rho RT/M$ where M is the molecular weight of the gas. Hence (1) yields

$$-dp = g\frac{pM}{RT}dz, \quad . \quad . \quad . \quad . \quad (2)$$

or

$$\int\frac{dp}{p} = -\frac{gM}{R}\int\frac{dz}{T} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Assuming T to be constant, which is far from being the case as far as the troposphere is concerned, we get on integrating (3) the result

$$p = p_0 e^{-gMz/RT} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This is known as Laplace's formula and gives the pressure p at the height z in terms of the pressure p_0 at the earth's surface.

As the temperature of the air column is really not constant, in actual practice the mean temperature of the air column is substituted in equation (4). This equation can then be readily applied to calculate the difference in height between two stations when the barometric pressures at the two stations are known.

For calculating the distribution of pressure in the stratosphere we have to apply equation (4) to each constituent separately since due to variation in composition M does not remain the same at all heights. We therefore obtain for the partial pressures the result

$$p = p_0 e^{-gMz/RT} \;;\; p' = p_0' e^{-gM'z/RT} \quad . \quad . \quad . \quad (5)$$

and the total pressure is the sum of these partial pressures.

5. Convective or Adiabatic Equilibrium.— We have already seen in § 3 that the troposphere is mainly in convective equilibrium. Hence

equation (4) which was deduced on the assumption that the atmosphere is at rest is not quite correct. The factor which really determines the distribution of the atmosphere is not equalisation of temperature as assumed in § 4 but the condition that a given mass of gas on being moved from one place to another, shall take up the requisite volume and pressure in its new position without any loss or gain of heat by conduction. The law connecting the volume and pressure in the troposphere should on such assumption approximate to the adiabatic law.

If the adiabatic law $p = c\rho^{\gamma}$ holds for the atmosphere, we have

$$\frac{dp}{dz} = c\gamma\rho^{\gamma-1}\frac{d\rho}{dz}.$$

Hence from (1) we get

$$c\gamma\rho^{\gamma-1}\frac{d\rho}{dz} = -g\rho.$$

Integrating this we get

$$\frac{c\gamma}{\gamma-1}(\rho_0^{\gamma-1} - \rho^{\gamma-1}) = gz, \qquad . \quad . \quad . \quad (6)$$

where ρ_0 is the density at zero level. This is the law according to which the density should fall off with increase in height in the troposphere. Since $p = \rho RT/M$, we get on substitution in the relation $p = c\rho^{\gamma}$ the result

$$T = \frac{cM}{R}\rho^{\gamma-1}.$$

Substituting this in (6) we obtain

$$\frac{\gamma}{\gamma-1}\frac{R(T_0-T)}{M} = gz,$$

where T_0 is the temperature at height zero, and J the mechanical equivalent of heat. Now since $\gamma = c_p/c_v$ and $JM(c_p - c_v) = R$, the above relation yields*

$$\frac{T_0-T}{z} = \frac{g}{Jc_p} = \frac{1}{10293}. \qquad . \quad . \quad . \quad . \quad (7)$$

Thus the temperature decreases proportionately to the increase of height as we go upwards in the atmosphere. Substituting numerical values we find that the constant of the above equation is about 10°C per km. This value is about twice the experimentally observed temperature gradient, namely 5°C. per km.

WATER VAPOUR IN THE ATMOSPHERE

6. Hygrometric State of air.— Water gets into the atmospheric air on account of evaporation from surfaces of oceans, rivers, lakes,

* This could be obtained more readily by using equation (25), p. 48 in place of equation (23)

snow-covered mountains, moist soil and from various other sources. Evaporation depends upon a number of factors, namely, the temperature of the air, the wind velocity, the pressure and the amount of moisture the air already contains. Increase of temperature and of wind velocity increases the rate of evaporation while increase of pressure and of moisture in the atmosphere decreases it. But the capacity of the air to hold water vapour is limited and depends upon temperature only. At a temperature t, air can hold only a certain amount of water vapour which is given by the saturated vapour pressure corresponding to the temperature t, and this amount increases with increase of temperature. In Table 1 we give the saturated vapour pressure of water at different temperatures and the values are

Table 1.—Maximum vapour pressure of water in millimetres of mercury at different temperatures.

Temp. °C.	0	1	2	3	4	5	6	7	8	9
0	4·579	4·926	5·294	5·685	6·101	6·543	7·013	7·513	8·045	8·609
10	9·209	9·844	10·52	11·23	11·99	12·79	13·63	14·53	15·48	16·48
20	17·54	18·65	19·83	21·07	22·38	23·76	25·21	26·74	28·35	30·04
30	31·82	33·70	35·66	37·73	39·90	42·18	44·56	47·07	49·69	52·44
40	55·32	58·34	61·50	64·80	68·26	71·88	75·65	79·60	83·71	88·02
	0	2	4	6	8	10	12	14	16	18
50	92·51	102·1	112·5	123·8	136·1	149·4	163·8	179·3	196·1	214·2
70	233·7	254·9	277·2	301·4	327·3	355·1	384·9	416·8	450·9	487·1
90	525·8	567·0	610·9	657·6	707·3	760·0	815·9	875·1	937·9	1004·4

plotted in Fig. 2, p. 321. If the air contains the maximum amount of water vapour that it can hold, it is saturated ; if it contains a lesser amount, it is unsaturated. In some cases, it may contain more than the equilibrium quantity ; it is then called supersaturated. The amount of water vapour held in air may be expressed in grams per cubic metre or in terms of pressure in millimetres which it exerts. This is known as the '*Absolute Humidity*' of the air. Humidity thus conveys information regarding quantity of water vapour in the atmosphere. The state of the atmosphere with regard to its actual water content is generally expressed by its Relative Humidity, which is the ratio of the actual quantity of water vapour present in a given quantity of air to the maximum quantity that it could hold if it were saturated at the observed temperature. Relative humidity is always expressed in percents. Thus the hygrometric state of air *i.e.*, its moisture content and its capacity to hold moisture, can be fully specified by stating its temperature and relative humidity.

7. Dew-point.— If air containing moisture is progressively cooled, a temperature will be reached at which the moisture that it contains

is sufficient to saturate it. This temperature is called the *Dew-point.* Any further cooling of the air will bring about a deposition of moisture on the surface of the containing vessel in the form of "dew". In the large-scale phenomena occurring in the atmosphere the deposition may take any one of the different forms, *viz.*, fog, cloud, rain, frost, hail, snow, dew, etc. It is easily seen that the four quantities—temperature, absolute humidity, relative humidity and dew-point are inter-related and a determination of only two of them is sufficient.

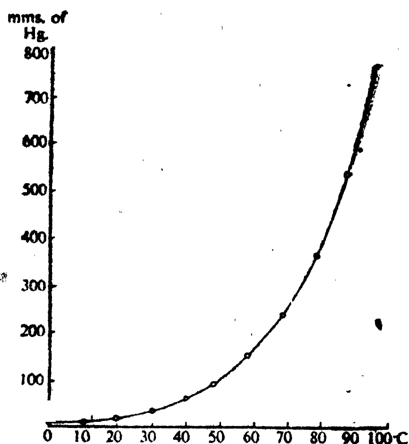


Fig. 2.—Vapour pressure curve of water.

This can be easily done with the help of Table 1. Thus if the temperature and the dew point are 30° and 20°C. respectively, the saturated vapour pressure at 20°C, is 17·54 mm. which gives the absolute humidity of the air, and the relative humidity (R.H.) is (17·54/31·82)×100=55%. Conversely, if the absolute humidity is known to be 9·7 mm. the dew-point is seen from the table to be equal to 10°C, and the R.H.= (9·7/31·82)×100 = 30%.

8. Hygrometers.— The study and measurement of moisture present in the atmosphere is called *Hygrometry* and the instruments used for measuring the amount of moisture are called hygrometers (*Hygro* = moisture, *meter* = measurer). From what has beeen said above, it will be evident that besides temperature we need measure any one of the three quantities—absolute humidity, relative humidity and dew-point. This gives rise to a variety of hygrometers which may be broadly classified as follows :—(1) Absorption hygrometers such as the chemical hygrometer, (2) Dew-point hygrometers, (3) Empirical hygrometers such as the wet-and-dry bulb hygrometer and the hair hygrometer for which no complete theory has yet been worked out but which are by far the most important.

9. The Chemical Hygrometer.— Absolute humidity is directly found out by means of the chemical hygrometer. In this instrument a stream of air is aspirated slowly over drying tubes, and the gain in weight of the tubes and the volume of air passed over are recorded. Thus the mass of water vapour actually present in a given volume of air is found out, and this is compared with the mass required to saturate the same volume of air at the same temperature. This latter quantity is given in tables.

The disadvantages of this method are that the apparatus is large

and not easily portable, the experiment takes considerable time and laborious corrections must be applied. Its chief use is for standardising the simpler types of instruments in the laboratory.

10. Dew-point Hygrometers.— Hygrometers in which humidity is found from a direct determination of the dew-point are called Dew-point Hygrometers. Examples of this type are the Daniell, the Regnault and the Dines' hygrometers. The essential principle underlying all of them is the same, *viz.*, a surface exposed to air is steadily cooled till moisture in the form of dew begins to deposit on it. The temperature is again allowed to rise till the dew disappears. The mean of the two temperatures at which the dew appears and disappears gives the dew-point. These hygrometers are however rarely used in meteorological work. They differ from one another in the manner of cooling or in the nature of the exposed surface. We shall therefore describe only one of them, *viz.* the Regnault's hygrometer.

11. Regnault's Dew-point Hygrometer.— This consists of a glass tube fitted with a thin polished silver thimble S (Fig. 3) containing ether. The mouth of the tube is closed by a cork through which passes a long tube going to the bottom of the ether, a thermometer with its bulb dipping in the ether, and a short tube T connected on the outside to an aspirator. When the aspirator is in action air is continuously drawn through the ether producing a cooling and the temperature of the thermometer falls. The process is continued till moisture deposits on the surface of the thimble, and the corresponding temperature is noted. In order to help in recognizing the first appearance of this moisture by comparison, a second similar tube provided with a silver thimble S but without ether is placed beside it. Next the aspirator is stopped, the apparatus allowed to heat up and the temperature when the dew disappears is noted. The mean of these two temperatures gives the dew-point. The dew-point hygrometer has the following disadvantages:—(1) It is difficult to determine the instant when dew appears, (2) the temperature of the thermometer does not accurately represent the temperature of the surface, (3) the instrument should be used in still air, (4) the observer himself, being a source of water vapour, is likely to disturb the readings. Attempts have been made to minimise or eliminate these difficulties, but it is not possible to get continuous records from such instruments.

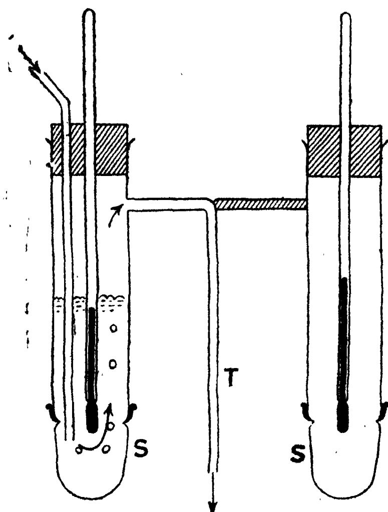


Fig. 3.—Regnault's Dew-point Hygrometer.

12. The Wet and Dry Bulb Hygrometer or Psychrometer— "Relative Humidity" can be easily measured by means of a wet and dry bulb hygrometer. This consists of two accurate mercury thermometers suitably mounted on a frame. Round the bulb of one of these is tied a piece of muslin to which is attached a wick extending down into a vessel containing pure water. The evaporation from the large surface exposed by the muslin produces a cooling and thus the wet bulb thermometer records a lower temperature than the dry bulb thermometer. In the steady state there is a thermal balance between the wet bulb and the surroundings. The greater the evaporation the greater will be the difference in temperature between the two. Now evaporation will be greater the lesser the humidity of the air and thus the difference in temperature between the wet bulb and the dry bulb is a direct measure of the humidity. The rate of evaporation is, however, further affected by the pressure and the wind; large pressure tends to retard evaporation while large wind velocity accelerates it. The effect of pressure is however very small and may be neglected, while the effect of wind is rendered constant by maintaining a constant supply of fresh air.

A relation between the readings of the two thermometers and certain other quantities can be easily found. If, T, T' denote the absolute temperatures of the dry and wet bulbs respectively, p the pressure of water vapour prevailing in the air and p' the saturated vapour pressure at T', and H the barometric pressure, the rate of evaporation will be proportional to $\frac{p'-p}{H}$ and also to $(T-T')$; therefore

$$p'-p = AH\ (T-T'), \qquad \text{(8)}$$

where A is some constant depending upon the conditions of ventilation and is determined from a large number of experiments. In actual practice Hygrometric Tables have been prepared by the Meteorological Office assuming the value of A for a fixed draught of air. From these tables the pressure p of water vapour prevailing in the air can be directly read if the dry bulb temperature and the difference between the dry and wet bulb temperatures are known. Knowing p the relative humidity can be found.

13. The Hair Hygrometer.— For ordinary purposes the relative humidity can be roughly measured by the Hair Hygrometer. This consists essentially of a long human hair from which all oily substance has been extracted by soaking it in alcohol or a weak alkali solution (NaOH or KOH). When so treated the hair acquires the property of absorbing moisture from the air on being exposed to it and thereby changing in length. Experiments have shown that this change in length is approximately proportional to the change, between certain limits, in the relative humidity of the atmosphere. Fig. 4 shows a

hair hygrometer. The hair *h* has its one end rigidly fixed at A while the other end passes over a cylinder and is kept taut by a weight or spring. The cylinder carries a pointer which moves over a scale of relative humidity graduated from 0 to 100. The changes in length of the hair due to changes in humidity tend to rotate the cylinder and thereby cause a motion of the pointer. The instrument must be frequently standardized by comparison with an accurate hygrometer and then its readings are reliable to within 5%.

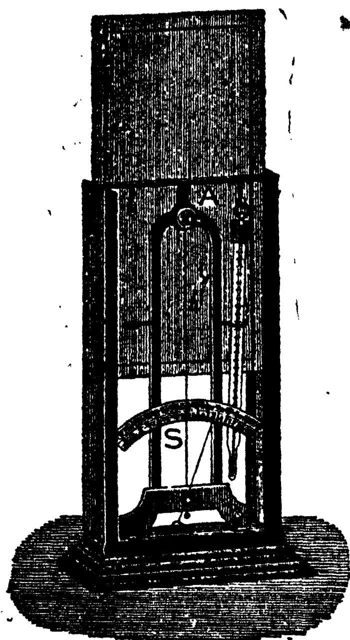


Fig. 4.—The hair hygrometer.

14. Methods of Causing Condensation.— We shall now find out under what conditions the water vapour present in the atmosphere can be precipitated from it. This water vapour can be condensed into liquid water or solid ice if the actual vapour pressure exceeds the maximum vapour pressure corresponding to the existing temperature. This happens almost exclusively when the air is cooled down more or less suddenly but in rare cases it may occur if the vapour pressure happens to increase due to some local effects such as compression of saturated water vapour etc.

The cooling of air may take place by the following three processes:—

(1) Due to radiation of heat or due to contact with cold bodies.

(2) Due to the mixing of cold and warm air masses.

(3) Due to adiabatic expansion caused by sudden decrease of pressure.

The first process should have been the most effective in producing precipitation had it been active in large masses of air. But air even when it is moist, is a poor conductor and radiator of heat, so that radiation and conduction of heat play a minor role in the phenomenon of precipitation. The result of the loss of heat by radiation or by contact with cold bodies, such as the surface of the earth in winter, cold walls, stones, etc., is the formation of mist, fog, dew, etc.

The second mode of condensation depends essentially on the experimental fact that the saturated vapour pressure of water increases much more rapidly with increase of temperature than the temperature itself. Thus if two equal masses of air, initially saturated at tem-

peratures t and t' respectively, are allowed to mix together, they will acquire the mean temperature $t_m = (t+t')/2$, while the mean vapour pressure will be $(e+e')/2$, where e, e' denote the saturated vapour pressure of water at temperatures t and t' respectively. On account of the above property, however, this mean vapour pressure will be greater than E, the saturated vapour pressure at t_m and therefore the excess of water will condense. As an example take the following illustration:—Let us have equal masses of saturated air at 4° and 32°C. When mixed up the temperature becomes 18°C. To saturate the mass we require 15·4 gm. per cubic metre. The separate masses contain 6·4 and 33·8 grams and the mixture $\frac{6 \cdot 4 + 33 \cdot 8}{2}$ gm. per cubic metre. Hence $20 \cdot 1 - 15 \cdot 4 = 4 \cdot 7$ gm. will separate by condensation.

If the two masses of air are not saturated before mixing, there may be condensation in some cases. This will depend upon the proportions of the mixture. If both the masses are very near the point of saturation, then condensation may take place at some places, and no condensation or even evaporation at others. This explains the formation and the disappearance of certain kind of clouds.

This third process is the most important because it is active on a large scale and produces cloud and rain. When moist air is allowed to expand adiabatically its temperature falls and some of its moisture is condensed if the temperature falls below the dew-point. This is the process which generally takes place in the atmosphere. An ascending current of moist air suffers a decrease of pressure as it ascends ; it therefore expands almost adiabatically and parts with some of its moisture. To calculate the cooling we have to apply the first law of thermodynamics.

15. Adiabatic Change of Humid Air.—From the first law of thermodynamics if dQ be the amount of heat supplied to a given mass of air,

$$dQ = c_p\,dT - \frac{v}{J}\,dp = c_p\,dT - \frac{RT}{MpJ}\,dp. \qquad (9)$$

In case of a mass of saturated air rising upwards, the heat dQ is added as a result of an amount dm of vapour being condensed. Hence,

$$dQ = -L\,dm, \qquad (10)$$

where L is the latent heat of vaporization. Therefore

$$-L\,dm = c_p\,dT - \frac{RT}{MpJ}\,dp. \qquad (11)$$

The total mass m of water vapour in the air per c.c. is given by

$$m = 0 \cdot 623\,\frac{e}{p} \times \rho,$$

where 0·623 is the ratio of the molecular weight of water vapour to the weighted mean of the molecular weight of the constituents of dry air, e the vapour pressure, and p the pressure of the dry air and ρ its density. Hence

$$\frac{dm}{m}=\frac{de}{e}-\frac{dp}{p}. \qquad (12)$$

Substituting this value of dm in (11), we have

$$-Lm\frac{de}{e}+\frac{Lm}{p}\,dp-c_p dT+\frac{RT}{MpJ}dp=0,$$

or,

$$\left(c_p+Lm\frac{de}{e}\frac{1}{dT}\right)dT=\frac{dp}{p}\left(Lm+\frac{RT}{JM}\right). \qquad (13)$$

Now $dp=-\rho g dz=-\frac{gMp}{RT}dz$. Substituting this value in (13) we get

$$\frac{dT}{dz}=-\frac{g\left(\frac{LmM}{RT}+\frac{1}{J}\right)}{c_p+\frac{Lm}{e}\frac{de}{dT}} \qquad (14)$$

This is the rate of decrease of temperature with elevation of saturated air. All the quantities on the right-hand side of this equation are known, so that $\frac{dT}{dz}$ can be easily evaluated.

Books Recommended.

1. Humphreys, *Physics of the Air.*
2. Brunt, *Meteorology.*
3. Lempfert, *Meteorology.*
4. Hann, *Lehrbuch der Meteorologie.*
5. Wegener, *Thermodynamik der Atmosphere.*

APPENDIX I

ERRORS OF MERCURY THERMOMETER AND THEIR CORRECTION

As mentioned on p. 2 various corrections must be applied to the mercury thermometer if it is used for accurate work. The method of applying these corrections is explained below:—

(*i*) *Secular Rise of Zero.* Glass is to some extent plastic and therefore its recovery to its original volume is an extremely slow process. During the construction of the thermometer the glass is heated to high temperatures and then allowed to cool. In this cooling process the contraction of the glass first takes place rapidly and then slowly even upto several years. Naturally therefore when calibration of the thermometer is usually undertaken the glass has not contracted to its final steady volume and the zero-point shows a secular rise for years due to this gradual contraction. This defect can be greatly removed by choosing suitable material for the glass of the thermometer, by properly annealing the tubes and storing them for years before making thermometers out of them.

(*ii*) *Depression of Zero.* This defect is also due to the defect in the property of glass mentioned above. When a thermometer is suddenly cooled from 100° to 0°C, the bulb does not at once regain its original volume and there is a consequent depression of zero, whose magnitude is greater the higher the temperature to which the thermometer was exposed and the longer the duration of this exposure. The method adopted by the Bureau International to correct for the depression of zero is the "*movable-zero method*" of reading temperatures. In this method the boiling point (100°C) is first determined and immediately after, the ice reading is taken ; let these readings on the thermometer be X and Z respectively. Suppose this thermometer reads X_t when immersed in a bath at t°C. Immediately after this the thermometer is immersed in ice ; let its corresponding reading be Z_t. Then the correct temperature t°C of the bath is given by

$$t = \frac{X_t - Z_t}{X - Z} 100.$$

(*iii*) *Errors in the fixed points.* For the lower fixed point the thermometer is clamped vertically with the bulb and a little part of the stem surrounded by pure ice mixed with a little quantity of distilled water. Suppose in the steady state the mercury stands at −0·1°C; then the freezing point correction is +0·1°C (additive). If the level of mercury stands above the zero degree mark, the correction is subtractive.

For the upper fixed point the thermometer is kept suspended inside a hypsometer with the bulb exposed to steam in the inner chamber. The steady reading of the mercury level is observed and the reading of the manometer indicating the pressure of steam noted. Suppose the thermometer reads 99·2°C under a pressure of 75·8 cm

of mercury. Since the boiling point for this pressure is 99·93°C, the correction is $99{\cdot}93 - 99{\cdot}2 = 0{\cdot}73$°C and is positive. If the observed boiling point is above the calculated one, the correction is negative.

(*iv*) *Correction for non-uniformity of bore.* As capillary tubes are drawn and not bored, slight inequalities in the diameter of the bore are bound to exist in the stem of the thermometer. This necessitates a small correction which is carried out as follows:—A small portion of the mercury thread is detached from the rest and its length measured when it occupies successively different parts of the stem, say between 0 and 10, 10 and 20, . . . 90 and 100 marks. The measured lengths will vary from place to place due to non-uniformity of the bore ; let these lengths be l_1, l_2, ... l_{10} respectively. Let the corrections to be made for non-uniformity in the vicinity of the 0, 10, ... 100 mark be a_0, a_{10} . . . a_{100} respectively. If l is the accurate length of the mercury thread used,

$$l = l_1 + a_{10} - a_0 \quad . \quad . \quad . \quad . \quad (1)$$

$$l = l_2 + a_{20} - a_{10} \quad . \quad . \quad . \quad . \quad (2)$$

$$l = l_{10} + a_{100} - a_{90} \quad . \quad . \quad . \quad . \quad (3)$$

Adding up,

$$10\,l = (l_1 + l_2 + \ldots\ldots l_{10}) + (a_{100} - a_0). \quad . \quad . \quad . \quad (4)$$

a_{100} and a_0 are the corrections to the upper and lower fixed points which can be determined experimentally as explained in (*iii*) above. Hence l can be calculated from (4). Substituting this value of l in (1) a_{10} can be calculated since a_0 is known. Similarly from (2) a_{20} is calculated and so on. A graph is then drawn with the marked scale divisions as abscissa, and a_0, a_{10}, ... a_{100} as ordinate. From this graph corrections for intermediate temperatures can be easily read.

In standard English thermometers this tedious correction has not to be applied by the user as the interval between the fixed points is subdivided not into equal parts but into equal volumes to represent the degrees on this thermometer.

(*v*) *Correction for lag of the thermometer.* If the bulb of a thermometer is placed in a hot bath, the thermometer will not attain the temperature of the bath instantaneously but will require a small, definite interval of time to attain that temperature. This is called the "lag" of the thermometer. The lag of the mercury thermometer increases with the mass of mercury and the thickness of the glass and also depends upon the nature of the medium surrounding the bulb. Due to this lag the thermometer reading will be higher when a bath is cooling and lower when the bath temperature is rising.

Suppose we consider the case when the temperature of the bath is rising. The correction for lag is applied as follows:—The bulb of the thermometer is immersed in the bath and the thermometer readings noted as a function of time and the observations plotted on a graph with temperature as ordinate and time as abscissa (Fig. 1). The curve AB represents the rise of temperature with time. To

find the correct temperature of the bath at each point on the curve, an auxiliary experiment is performed in which the bulb of the thermometer is immersed in a thermostatic bath maintained at a temperature somewhat higher than the maximum recorded in the main experiment. The thermometer readings are read at short intervals until the thermo-

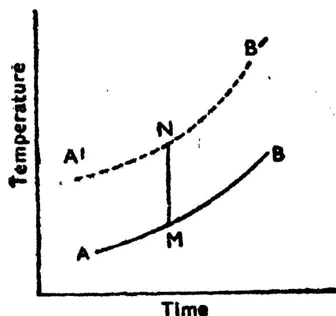


Fig. 1

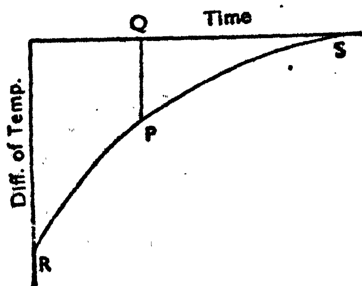


Fig. 2

meter attains the steady temperature of the bath. These readings are plotted on a graph with time as abscissa and the difference of the thermometer reading and the temperature of the bath as ordinate, and the curve RS (Fig. 2) obtained.

It will now be assumed that the lag does not depend upon the actual temperature of the bath but only upon the rate at which the temperature is changing. Consider a point M on the main curve. The lag at this instant depends upon the slope ($d\theta/dt$) of the curve at this point M. Now find out a point P on the curve RS where the slope is the same as the slope at the point M. Then the lag PQ will also be the lag at M. Hence if PQ = MN, N gives the correct temperature corresponding to M. In this way the corrected curve A'B' can be easily drawn.

(vi) Error due to changes in the size of the bulb caused by variable internal and external pressure. For diminishing the time lag the bulb of the thermometer is usually made thin. Any increase in external pressure therefore easily alters the volume of the bulb and causes a rise of mercury level in the stem. Suppose the thermometer is graduated when the external pressure is equal to the atmospheric pressure. If the external pressure is now increased the bulb will contract and the mercury in the stem will rise. The *external pressure coefficient* is defined as the ratio of the rise of mercury in the stem, expressed in degrees, to the increase in external pressure, expressed in mm. of mercury. This ratio can be easily determined experimentally. Knowing this and the external pressure to which the bulb is subjected at the time of reading the thermometer, the correction to be applied can be readily calculated.

When a thermometer has been graduated in the horizontal position and a subsequent reading is taken with the thermometer in the vertical position, there is an increase in the internal pressure due to the vertical column of mercury in the thermometer. The bulb con-

sequently expands causing a depression of mercury in the stem, for which a correction is necessary. To determine this correction the readings of the thermometer are observed in the horizontal and vertical positions at any one temperature. The difference in the two readings gives the depression of mercury in the stem due to an increase in pressure caused by the mercury column which extends from the centre of the bulb to the mark on the thermometer at which mercury stood in the vertical position of the thermometer. Expressing this pressure in mm. of mercury we can define the *internal pressure coefficient* as the ratio of the depression of mercury in the stem, expressed in degrees, to this increase of internal pressure. Knowing this coefficient, which is constant, the correction can be calculated for any reading of the thermometer in the vertical position.

(*vii*) *Error due to capillarity.* The surface tension of mercury causes an excess of pressure within the meniscus over that outside. This excess pressure depends on the radius of the tube at the point where the meniscus lies ($p \propto 1/r$). If the stem is not uniform in bore, there will be variations of internal pressure as the thread of mercury rises or falls and therefore the thermometer readings will not be very accurate. Further the angle of contact between mercury and the sides of the tube depends upon whether the mercury is rising or falling, the meniscus being flatter when mercury is falling. Therefore a rising thread always gives somewhat lower readings than a falling one. It is also found that the mercury thread is less disturbed by capillarity when it rises than when it falls and therefore it is preferable to take readings with a rising column.

(*viii*) *Error due to exposed stem or emergent column.* Generally when the temperature of a bath is measured, only the bulb of the thermometer and a portion of the stem are immersed in the bath. In such cases the part of the stem exposed to the atmosphere does not acquire the temperature of the bath and therefore the thermometer reading will be less than the true temperature of the bath. The correction for this exposed or emergent column is applied as follows:—Let the thermometer reading be t_1 when the stem upto t_2 mark is immersed in the bath. Thus n $(=t_1-t_2)$ divisions are exposed to the atmosphere, and its average temperature t_0 is measured by a special integrating thermometer with a long bulb placed near it, with its centre coinciding with the centre of the exposed part. Let t denote the corrected temperature and $\delta=m-g$ the coefficient of apparent expansion of mercury in glass (m = expansion coefficient of mercury, g, of glass). Then a mercury column whose length is n divisions at t_0 has to be corrected to the temperature t. If this column were to rise in temperature from t_0 to t, the increase of height (which measures the increase of volume) would be $n\delta(t-t_0)$ divisions. This must therefore be added to the observed reading t_1 to give t. Hence

$$t = t_1 + n\delta(t-t_0)$$

or

$$t = \frac{t_1 - n\delta t_0}{1-n\delta}.$$

EXAMPLES

I

1. Discuss the advantages of using one of the permanent gases as a thermometric substance for defining a scale of temperature. Describe some convenient and accurate form of gas thermometer, explain its mode of use and show how the temperature is calculated from the observations made with it. (Madras, B.Sc., 1925.)

2. The pressure of the air in a constant volume gas thermometer is 80·0 cm. and 109·4 cm. at 0° and 100°C. respectively. When the bulb is placed in some hot water the pressure is 94·7 cm. Calculate the temperature of the hot water.

3. An air bubble rises from the bottom of a pond, where the temperature is 7°C., to the surface 27 metres above, at which the temperature is 17°C. Find the relative diameters of the bubble in the two positions, assuming that the pressure at the pond surface is equal to that of a column of mercury of density 13·6 gm. per c.c. and 76 cm. in height.

4. Explain clearly the meaning of absolute temperature of the air thermometer scale. A gram of air is heated from 25°C to 70°C. under a constant pressure of 75 cm. of mercury. Calculate the external work done in the expansion given that the density of air at N.T.P. is 0·001293.

5. What is an air thermometer? Explain the method of measuring temperature by Callendar's compensated air thermometer. Describe a method for measuring very high temperatures. (A. U., B.Sc., 1927.)

6. Describe the Callendar's compensated thermometer and explain how temperatures are taken with it. (A. U., B.Sc., 1944; Utkal Univ. 1952; Punjab Univ. 1954.)

7. Describe briefly the method of standardisation and the range of usefulness of platinum resistance thermometers, and discuss some of the difficulties of precise resistance measurement and the precautions to be taken to avoid or correct for these. (A. U., B.Sc., Hons., 1929.)

8. Give an account of the construction and use of the platinum resistance thermometer, pointing out any special advantages of the instrument. (Utkal Univ. 1950; Gujerat Univ. 1951; Punjab Univ. 1956.)

9. Describe various methods of measuring high temperatures. (A. U., B.Sc., 1931, 1932, 1949; Gujerat Univ. 1951; Punjab Univ., 1956.)

10. State, with reasons, the type of temperature measuring device which you consider most suitable for use at temperatures, of (*a*) −200°C., (*b*) −50°C., (*c*) 50°C., (*d*) 700°C., (*e*) 2000°C. (London, B.Sc.)

11. Describe two methods for measuring high temperatures. State clearly the principles underlying them and the range and sensitivity of each. (A. U., B.Sc., 1941.)

12. Write a short essay on the measurement of (*a*) high and (*b*) low temperatures. (Delhi Univ. 1954; Punjab Univ., 1946.)

13. In what respects is a constant volume gas thermometer superior to the constant pressure gas thermometer. Describe the construction and use of the international standard hydrogen constant volume thermometer. (Patna Univ., 1949; Utkal Univ., 1954.)

II

1. Enunciate Newton's law of cooling and show how corrections can be made for the heat lost by radiation during calorimetric experiments. Establish a relation for finding the specific heat of liquids by the method of cooling. (Nagpur, B.Sc., 1930.)

2. If a body takes 3 minutes to cool from 100°C. to 60°C., how long will it take to cool from 60°C. to 20°C., assuming that the temperature of the surroundings is 10°C., and that Newton's law of cooling is obeyed.

3. Describe Joly's differential steam calorimeter and explain how it is used for finding the specific heat of a gas at constant volume. State the corrections to be made. (Punjab Univ., 1952, 1954; Gujerat Univ., 1951; Patna Univ., 1947.)

4. Describe the steam calorimeter. Explain how it may be used to determine (*i*) the specific heat of a gas at constant volume, (*ii*) the specific heat of a small solid. (A. U., B.Sc., 1929.)

5. Describe a method of determining the specific heat of a gas at constant volume, giving a neat diagram of the arrangement of the apparatus necessary. Why is the specific heat at constant pressure greater than that at constant volume? (Dacca B.Sc., 1930.)

6. Describe the constant flow method of Callendar and Barnes for the measurement of the mechanical equivalent of heat. In an experiment using this method, when the rate of flow of water was 11 gm. per minute, the heating current 2 amperes and the difference of potential between the ends of the heating wire 1 volt, the rise of temperature of the water was 2·5°C. On increasing the rate of flow to 25·4 gm. per minute, the heating current to 3 amperes and the potential difference between the ends of the heating wire to 1·51 volts, the rise of temperature of the water was still 2·5°C. Deduce the value of the mechanical equivalent of heat (A. U., B.Sc., 1931.)

7. Describe Nernst vacuum calorimeter and indicate briefly how it has been used for measuring specific heats at low temperatures. (A. U., M.Sc., 1925.)

8. Give an account of the continuous flow method of measuring the specific heat of a gas at constant pressure and point out its advantages. (A. U., B.Sc., 1938.)

9. In a determination of the specific heat at constant pressure by Regnault's method the gas is supplied from a reservoir whose volume is 30 litres at 10°C. The pressure of the gas in the beginning is 6 atmos. and in the end 2 atmos., the temperature remaining constant at 10°C. The gas was heated to 150°C. and led into a calorimeter at 10·0°C. The final temperature of the calorimeter and contents was 31·5°C. and its water equivalent was 210 gm. If the density of the gas is 0·089 gm. per litre at N. T. P., calculate its specific heat at constant pressure.

10. A quantity of air at normal temperature is compressed (*a*) slowly, (*b*) suddenly, to $\frac{1}{10}$ of its volume. Find the rise of temperature if any, in each case.

[Ratio of the two specific heats of air = 1·4, log 2·73 = ·4362; log 6·858 = 0·8362.]

Deduce the formula used for (*b*). (A. U., B.Sc., 1928.)

11. In a Wilson apparatus for photographing the tracks of α particles the temperature of the air is 20°C. If its volume is increased in the ratio 1·375 : 1 by the expansion, assumed adiabatic, calculate the final temperature of the air. (The ratio of specific heats of air = 1·41.)

12. What is meant by an "isothermal" and by an "adiabatic"? Find the relation between pressure and volume for a perfect gas in an adiabatic change. (London, B.Sc.)

13. Deduce from first principles the adiabatic equation of a perfect gas.

A motor car tyre is pumped up to a pressure of two atmospheres at 15°C. when it suddenly bursts. Calculate the resulting drop in the temperature of air. (A. U., B.Sc., 1938.)

14. Describe a method of determining the ratio of the specific heats of a gas at constant pressure and constant volume. How has the mechanical equivalent of heat been calculated from a knowledge of this ratio? (A. U., B.Sc., 1929.)

15. Explain why the specific heat of a gas at constant pressure is greater than that at constant volume. Obtain an expression for the difference between the values for a perfect gas. Find the numerical value of their ratio for monatomic gases. (Punjab Univ., 1949, 1951; Utkal Univ., 1952.)

16. Describe the Clement & Desormes' method of finding the ratio of specific heats of air, giving the simple theory of the method. What are the objections to the method and what modifications and improvements have been proposed. (A. U., 1950; Bihar Univ. 1954; Utkal Univ. 1955.)

17. Derive the relation between volume and temperature of a mass of perfect gas undergoing adiabatic compression.

A quantity of dry air at 15°C is adiabatically compressed to $\frac{1}{4}$th of its volume. Calculate the final temperature given $\gamma = 1{\cdot}4$ and $4^{0{\cdot}4} = 1{\cdot}74$. (Aligarh Univ., 1948; Punjab Univ., 1957.)

18. Explain how the mechanical equivalent of heat can be deduced from a knowledge of the specific heats of air at constant pressure and constant volume. State clearly any assumptions made in your reasoning and describe experiments, if any, which afford justification for such assumption. (Madras, B.Sc., 1925.)

19. Describe a method of determining the ratio of the two specific heats of a gas. Show that it follows from the kinetic theory of gases that the ratio of the two specific heats in the case of a monatomic gas is 1·66. (Madras, B.Sc., 1924.)

20. Find the ratio of the specific heats of a gas from the following data:—A flask of 10 litres capacity weighs, when exhausted, 160 gm.; filled with the gas at a pressure of 75 cm. of mercury it weighs 168 gm. The column of the gas, which when confined in a tube closed at one end and maintained at the same temperature as the gas in the flask, responds best to a fork of 223·6 vibrations per second, is 50 cm.

21. Determine the ratio of the specific heats of air from the following data:—Velocity of sound = 34215 cm. per sec. in air at 750 mm. and 17°C; density of air = ·00129 gm. per c.c. at N. T. P.; coefficient of expansion of air = $\frac{1}{273}$; $g = 981$ cm./sec.^{2}; density of mercury = 13·6 gm. per c.c. (Manchester, B.Sc.)

III

1. In an experiment with Joule's original apparatus the mass of the weights on either side was 20 kilograms and each fell through a distance of one metre forty times in succession. The water equivalent of the calorimeter and its contents was 6 kilograms and the rise in temperature during the experiment was 0·62°C. Calculate the value of the mechanical equivalent of heat.

2. Determine the heat produced in stopping by friction a fly-wheel 50 kilograms in mass and 50 cm. in radius, rotating at the rate of one turn per second assuming the fly-wheel to be a disc mounted axially and having a uniform distribution of mass.

3. A canon ball of 100 kilograms mass is projected with a velocity of 400 metres per second. Calculate the amount of heat which would be produced if the ball were suddenly stopped.

4. In one hour a petrol engine consumes 5 kilograms of petrol whose calorific value is 10,000 cals. per gram. Assuming that 23 per cent of the total heat escapes with the exhaust gases and that 12 per cent of the heat is converted into mechanical energy, find the average horse-power developed by the engine and the initial rate of rise of temperature of the engine per minute. Radiation losses may be ignored and the water equivalent of the whole engine is 40 kilograms.

5. Give the outlines of the methods by which the mechanical equivalent of heat can be determined. Assuming that for air at constant pressure the coefficient of expansion is 1/273, the density

at 0°C. and atmospheric pressure is 0·001293, the specific heat $_p$ = 0·2389 and the ratio c_p/c_v = 1·405, calculate the mechanical equivalent of heat. Suppose that there is inappreciable cohesion between the molecules. (Bombay, B.Sc., 1924).

6. Define the mechanical equivalent of heat. If the kinetic energy contained in an iron ball, having fallen from rest through 21 metres, is sufficient to raise its temperature through 0·5°C., calculate a value for the mechanical equivalent of heat (given g = 980 cm. per sec. per sec. and specific heat of iron = 0·1).

7. Show how the method of electrical heating has been adopted in the determination of the mechanical equivalent of heat. One gram of water at 100°C. is converted into saturated vapour at the same temperature. Calculate the heat equivalent of the external work done during the change. Density of water at 100°C. = 0·958 gms. per c.c.; density of saturated steam at 100°C. = 0·000598 gms. per c.c

8. Describe Callendar & Barnes' continuous flow method of measuring the mechanical equivalent of heat. State how the method can be adopted to measure the variation of specific heat of water between 10°C and 90°C. (Punjab Univ., 1951 ; A. U., 1951).

9. Explain what is meant by the "velocity of mean square" of the molecules of a gas and their "mean free path". Show how these two quantities can be found. (Bombay, B.Sc., 1924).

10. Calculate the molecular velocity (square root of the mean square velocity) in the case of a gas whose density is 1·4 gm. per litre at a pressure of 76 cm. of mercury. Density of mercury = 13·6, g = 981 cm. per sec. per sec. (Manchester, B.Sc.).

11. Show that pressure of a gas is equal to two-thirds of the kinetic energy of translation per unit volume. Calculate the kinetic energy of hydrogen per gram-molecule at 0°C. (A. U., B.Sc., 1949).

12. Deduce Boyle's and Avogadro's laws from the kinetic theory of gases. What interpretation of temperature is given according to this theory? (A. U., B.Sc., 1928.)

13. Outline the essential features of the kinetic theory of gases. Find an expression for the pressure of a gas on the basis of the kinetic theory. (Punjab Univ., 1954, 1955, 1957; Delhi Univ., 1954.)

14. Deduce an expression for the conductivity of a gas from the kinetic theory. How would you actually proceed to determine the conductivity of any particular gas? (A. U., B.Sc., Hons., 1931.)

15. State the law of equipartition of energy. Prove that for a monatomic gas, the value of gamma, the ratio between the specific heats is 5/3 and for a diatomic gas it is 7/5. (A. U., B.Sc., 1932.)

16. Find an approximate expression for the mean free path of a molecule in a gas, and give a short account of any one phenomenon depending on the length of the mean free path. (London, B.Sc., Hons.)

17. What is meant by (*a*) the "coefficient of viscosity" of a gas, (*b*) the "mean free path of its molecules"? Show how to deduce

a relation between these quantities from the kinetic theory. (Lond., B.Sc.)

18. Describe some phenomena which have led to the conclusion that molecules have a finite diameter and mean free path. How can the latter be determined?

IV

1. How has van der Waals modified the isothermal equation for a gas? Calculate the values of the critical pressure, volume and temperature in terms of the constants of his equation. How do the theoretically derived results tally with experiments? (A. U., B.Sc., 1931.)

2. Derive van der Waals' equation of state and obtain expressions for the critical temperature, pressure and volume in terms of the constants of van der Waals' equation. (Panjab Univ., 1957 ; Delhi Univ. 1953 ; Bombay Univ., 1953 ; Patna Univ. 1948 ; Calcutta Univ. 1948.)

3. Express the value of the critical temperature in terms of a, b and R. Calculate its value for CO_2 where $a = \cdot 00874$ and $b = \cdot 0023$. (Panjab Univ. 1957 ; Allahabad Univ. 1952.)

4. Define critical temperature, pressure and volume of a vapour and give some account of the behaviour of a substance near the critical point. (A. U., B.Sc., 1927.)

5. Draw a diagram showing the general form of the isothermal including both liquid and vapour state, and explain the meaning of the different parts of the curve. What is the true form of the straight portion of this curve and why? (A. U., B.Sc., 1935.)

6. Give an account of the properties of fluids in the neighbourhood of the critical point. Describe how you would determine the critical constants of a substance. (A. U., B.Sc., Hons., 1928.)

7. What is meant by the critical point in the state of a fluid? Show on a diagram the character of typical isothermals of a fluid above and below the critical temperature. Explain how van der Waals' equation accounts for the existence of a critical point. (London, B.Sc.)

8. Explain how van der Waals' equation accounts for the existence of a critical point. Calculate the values of the critical pressure, critical volume and critical temperature for a gas obeying van der Waals' equation. (A. U., B.Sc., 1947.)

9. Describe the experiments of Andrews on carbon dioxide. State and discuss the results obtained by him. (Bombay Univ., 1953 ; Baroda Univ., 1954.)

V

1. How would you determine the vapour pressure of a liquid above its normal boiling point? Explain how clouds are formed by the mixing of warm moist air with cold moist air. (A. U., B.Sc., 1927.)

2. Describe a method of determining the vapour density of a volatile liquid, and explain the theory of your method. (Dacca, B.Sc., 1928.)

3. Give an account of a method which has been adopted for the determination of the pressure of saturated vapour between 100°C., and 120°C. Explain clearly what is meant by the statement that the specific heat of saturated vapour at 100°C. is negative. (Madras, B.Sc., 1924.)

4. An electric current of 0·75 ampere is passed for 30 minutes through a coil of wire of 12·4 ohms resistance immersed in benzene maintained at its boiling point, and 29·85 gm. of benzene are found to have vaporised. Calculate the latent heat of vaporisation of benzene.

VI

1. Write an essay on 'artificial production of cold'. (A. U., B.Sc., Hons., 1930.)

2. Describe the manufacture of liquid air. (A. U., B.Sc., 1930.)

3. Discuss theoretically the production of cold by expansion of gases through porous plugs. How has this principle been applied in machines for liquefying air? (A. U., B.Sc., 1937 ; Delhi Univ., 1953, 1954.)

4. White a short essay on the liquefaction of the so-called permanent gases. (Dacca, B.Sc., 1928.)

5. Describe a method of liquefying hydrogen, and explain the principle involved in the process. (A. U., B.Sc., 1928.)

6. Describe and discuss the porous plug experiments of Joule and Kelvin. Explain what is meant by temperature of inversion, illustrating your answer by reference to hydrogen and helium. (London, B.Sc.)

7. Describe and explain the methods used in the manufacture of ice and liquid air. (A. U., B.Sc., 1935.)

8. Distinguish clearly between adiabatic change and Joule-Thomson effect. Describe how the latter has been utilised for liquefying hydrogen. (A. U., B.Sc., 1947.)

VII

1. Describe and explain a method of measuring the linear expansion of solids by means of interference bands.

2. If a crystal has a coefficient of expansion 13×10^{-7} in one direction and of 231×10^{-7} in every direction at right angles to the first, calculate its coefficient of cubical expansion. (London, B.Sc.)

3. A lump of quartz which has been fused is suspended from a quartz fibre and allowed to oscillate under the influence of the torsion of the fibre. If the coefficient of linear expansion of the material is 7×10^{-7} and the temperature coefficient of its rigidity is $+13 \times 10^{-5}$,

how many seconds a day or what fraction of a second a day would a change of temperature of 1°C. make? (London, B.Sc.)

4. A seconds pendulum is one which completes half an oscillation in 1 second. Such a pendulum of invar is given and is correct at 10°C. If the average temperature for the three months of June, July and August is 25°C. and the clock is correct at 12·0 a.m. on June 1st, how much will it be incorrect at 12·0 a.m. on September 1st? Coefficient of expansion of invar is 1×10^{-6}.

5. Describe, in full detail, the method by which the expansion of crystals, when heated, may be studied experimentally. (Allahabad Univ., 1943 ; Aligarh Univ., 1949 ; Panjab Univ., 1946, 1954.)

6. Describe a method by which the cubical expansion of a liquid can be accurately determined by weighing a solid of known expansion in it at two known temperatures.

A solid is found to weigh 29·9 gms. in a liquid of specific gravity 1·21 at 10°C. its weight in air being 45·6 gms. It weighs 30·4 gms. in the same liquid at 25°C when its specific gravity is 1·17. Calculate the cofficient of cubical expansion of the solid.

7. (*a*) Describe Regnault's method for the determination of the coefficient of absolute expansion of mercury. Indicate briefly the precautions adopted by Regnault to avoid errors.

(*b*) If the coefficient of cubical expansion of glass and mercury are $2{\cdot}5 \times 10^{-5}$ and $1{\cdot}8 \times 10^{-4}$ respectively, what fraction of the whole volume of a glass vessel should be filled with mercury in order that the volume of the empty part should remain constant when glass and mercury are heated to the same temperature. (Dacca, B.Sc., 1928.)

VIII

1. By what processes does hot water in an open vessel lose heat? Describe experiments by which the several causes of loss may be shown to exist. (Dacca, B.Sc., 1928.)

2. Define the thermal conductivity of a substance and describe some way of finding it.

An iron boiler 5/8 inch in thickness exposes 60 square feet of surface to furnace and 600 lbs. of steam at atmospheric pressure are produced per hour. The thermal conductivity of iron in inch-lb-sec. units is 0·0012 and the latent heat of steam is 536. Find the temperature of the underside of the heating surface. Explain why this is not the temperature of the furnace. (Dacca, B.Sc., 1929.)

3. Explain the difference between the thermal conductivity and the diffusivity of a substance.

The two sides of a metal plate 1·5 square metres in area, and 0·4 cm. in thickness are maintained at 100°C. and 30°C. respectively. If the thermal conductivity of the metal be 0·12 C.G.S. units find the total amount of heat that will pass from one side to the other in one hour. (Dacca, B.Sc., 1928.)

4. The interior of an iron steam-pipe, 2·5 cm. internal radius, carries steam at 140°C. and the thickness of the wall of the pipe is 3 mm. The co-efficient of emission of the exterior surface (heat lost per second per sq. cm. per degree excess) is 0·0003 and the temperature of the external air is 20°C. If the thermal conductivity of iron is 0·17 C. G. S. unit find the temperature of the exterior surface, and also how much steam is condensed per hour per metre length of tube, the latent heat of steam at 140°C. being 509. (London, B.Sc.)

5. The thickness of the ice on a lake is 5 cm. and the temperature of the air is $-10°C$. At what rate is the thickness of the ice increasing and approximately how long will it take for the thickness of the ice to be doubled?

(Thermal conductivity of ice = 0·004 cal. cm^{-1} sec^{-1} $°C^{-1}$. Density of ice = 0·92 gm. per c.c. Latent heat of ice = 80 cal. per gm.)

6. Define the terms conductivity and diffusivity as used in the theory of heat conduction. Describe a method of comparing the conductivity of two metal bars. Account for the fact that the evaporation of liquid air is greatly reduced when kept in a Dewar vacuum vessel. (Madras, B.Sc., 1924.)

7. Define conductivity. Deduce expression for the flow of heat in a long bar when it has acquired a steady state. (B. H. U., B.Sc., 1931.)

8. Define the coefficient of heat conductivity of a substance and give details of some method of determining this constant for iron. (A. U., B.Sc., 1931.)

9. Describe Ingen-Hausz's experiment, and prove from the mathematical theory that the conductivities of different bars vary as the square of the length up to which wax is melted. (A. U., B.Sc., 1945, 1950.)

10. Describe Forbes' method of determining the thermal conductivity of a metallic bar, and explain the formulæ used. (Lucknow Univ., 1950; Allahabad Univ. 1951; Punjab Univ. 1957, 1955, 1954.)

11. Define thermal conductivity. A steady stream of water flowing at the rate of 500 grams a minute through a glass tube 30 cms. long, 1 cm. in external diameter and 8 mm. in bore, the outside of which is surrounded by steam at a pressure of 760 mm., is raised in temperature from 20°C. to 30°C. as it passes through the tube. Find the conductivity of glass. You are given that log 1·25 = 0·223. Deduce any formula that you use. (A. U., B.Sc., 1937.)

12. Define thermal conductivity. Describe a method you have adopted in experimentally finding this constant for a good conductor. Find the coefficient of conductivity of a badly conducting material upon which the following experiment was made:—A very thin-walled hollow silver cylinder 40 cm. in diameter and 50 cm. in length is covered all over its external surface including the ends by a layer of the material 0·33 cm. in thickness. Steam at a temperature of 100°C. is passed through the cylinder and the external temperature is 20°C.

Water is found to accumulate within the cylinder at the rate of 3 gm. per minute. The latent heat of vaporization of water at 100°C. is 537 cal. per gram and cross-sections of the steam inlet and outlet are each 10 square centimetres. (Madras, B.Sc., 1925.)

13. Define conductivity and diffusivity of heat. When steam is passed through a circular tube of length l and having the internal and external diameters a and b respectively, prove that the radial flow of heat outwards is given by

$$2\pi Kl(\theta_1 - \theta_2)/\log_e \frac{b}{a}$$

where K is conductivity and θ_1, θ_2 the temperatures inside and outside the tube. How will you determine the conductivity of india-rubber? (A. U., B.Sc., Hons., 1930.)

14. Steam at 100°C. is passed through a rubber tube, 14·6 cm. length of which is immersed in a copper calorimeter of thermal capacity 23 cal. containing 440 gm. of water. The temperature of the water and calorimeter is found to rise at the rate of 0·019°C. every second when they are at the room temperature (22°C.). The external and the internal diameters of the tube are 1·00 cm. and 0·75 cm. respectively. Calculate the conductivity of india-rubber.

15. Prove that if a long bar is periodically heated at one end, the law of propagation of heat is given by the equation

$$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2}.$$

Obtain a solution of this equation and show how with its aid the diurnal and annual variation of temperature at some depth below the surface of the earth can be explained. (A. U., M.Sc., 1926.)

16. Heat is supplied to a slab of compressed cork 5 cm. thick and of effective area 2 sq. metres, by a heating coil spread over its surface. When the current in this coil is 1·18 amp. and the potential difference across its ends 20 volts, the steady temperatures of the faces of the slab are 12·5°C. and 0°C. Assuming that the whole of the heat developed in the coil is conducted through the slab, calculate the thermal conductivity of the cork.

17. Define coefficient of thermal conductivity and describe Lees' method for determining the thermal conductivity of metals (Punjab Univ., 1956, 1953.)

18. Describe Lees' method of determining the thermal conductivity of a bad conductor. (Bombay Univ., 1947.)

19. Describe and give the theory of a method useful for a practical determination of the thermal conductivity of a liquid. (London, B.Sc.)

20. Discuss some methods by which the thermal conductivity of a gas has been determined. What are the experimental difficulties and how have they been overcome?

21. How is the thermal conductivity of a liquid determined? How do you demonstrate that hydrogen is more conducting than air? (A. U., B.Sc., 1936.)

22. Discuss the difficulties which beset the investigation of the thermal conductivity of gases and indicate how and to what extent they have been overcome. (London, B.Sc.)

IX

1. What do you understand by a reversible cycle as opposed to an irreversible one? Give instances of each. (A. U. B.Sc., 1931.)

2. What is meant by a reversible change? Describe Carnot's cycle and prove that the efficiency of all reversible engines working between the same two temperatures depends only on the temperature of the hot and cold bodies. (Bombay Univ., 1948, 1949; Utkal Univ., 1954; Punjab Univ., 1953.)

3. Describe with diagrams an Otto engine and deduce an expression for its efficiency. (A. U., B.Sc., 1949.)

4. Describe some kind of internal combustion engine and explain fully how heat is thereby converted into work.

Describe its uses and applications and dwell upon its advantages over the steam engine. (A. U., B.Sc., 1927.)

5. Describe the cyclical process of a steam engine and compare its efficiency with that of an internal combustion engine. Explain (1) why steam engine is preferred in railways, and (2) why petrol engine is used in aeroplanes. (A. U., B.Sc., 1930.)

6. Write an essay on 'Heat engines'. (Dacca, B.Sc., 1929.)

7. Explain the indicator diagram and apply it to Carnot's cycle. Explain the conditions for reversible working and show that in general for reversible cycles $\int \frac{dQ}{\theta} = 0$. (Bombay, B.Sc., 1924.)

8. Describe Carnot's cycle. Show how the work done during each operation is represented on a *pv* diagram. Find an expression for the work done during each operation when the working substance is a perfect gas. (London, B.Sc.)

9. Discuss the statement: 'Reversibility is the criterion of perfection in a heat engine'. Explain with two examples what you understand by a reversible process.

A Carnot engine works between the two temperatures 100°C. and 10°C. Calculate its efficiency. (A. U., B.Sc., 1947.)

X

1. Show that when a body expands, the external work performed is given by the expression

$$\int_{v_1}^{v_2} p \, dv.$$

From the following data calculate what fraction of the specific heat of copper is due to the external work done in expansion in an atmosphere at a pressure of 76 cms. of mercury :—

Specific heat of copper = 0·093. Specific gravity of copper = 8·3, of mercury = 13·6. Coefficient of linear expansion of copper = 0·000016, $J = 4{\cdot}2 \times 10^7$ ergs per calorie. (A. U., B.Sc., 1929.)

2. Deduce an expression for the work required to compress adiabatically a mass of gas initially at volume v_1 and pressure p_1 to volume v_2.

Find the work required to compress adiabatically 1 gm. of air initially at N.T.P. to half its volume. Density of air at N.T.P. = 0·00129 gm./c.c. and c_p/c_v = 1·4 (Birm., B.Sc.)

3. Explain external and internal work. Discuss the changes in the kinetic energy of the molecules of a gas when heated and hence show that the ratio of the specific heats for a monatomic gas is 5/3.

4. Write an essay on the transformation into heat of other forms of energy. (Cal., B.Sc., 1928.)

5. In what sense can the second law of thermodynamics be regarded as furnishing an absolute scale of temperature? How can readings of gas thermometers be reduced to this particular scale? (A. U., B.Sc., Hons., 1931.)

6. Explain what you understand by a thermodynamic scale of temperature. Show that it agrees with an ideal gas scale. (Punjab Univ., 1954, 1956, 1957; Bombay Univ. 1953.)

7. Write notes on one of the following :—

(*a*) Lord Kelvin's absolute scale of temperature.

(*b*) Joule and Kelvin's porous plug experiment. (Nagpur, B.Sc., 1930.)

8. Calculate the change of entropy when 100 gms. of water at 30°C. are mixed with 200 gms. of water at 0° assuming that the specific heat of water is constant between these temperatures (London, B.Sc.)

9. Derive an expression for the entropy of a perfect gas in terms of its pressure, volume and specific heats. (Bombay, B.Sc., 1926.)

10. Prove that the increase of entropy per unit increase of volume under constant pressure is equal to the increase of pressure per unit increase of temperature during an adiabatic change. (Bombay B.Sc., 1926.)

11. Calculate the change of entropy when 10 gm. of steam at 100°C., cools to water at 0°, assuming that the latent heat of vaporisation is 536 and the specific heat of water is 1 at all temperatures.

12. State the second law of thermodynamics and apply it to the determination of the effect of pressure on the melting point of a solid. (A. U., B.Sc., 1928.)

13. Prove the thermodynamic relation

$$\left(\frac{d\phi}{dv}\right)_\theta = \left(\frac{dp}{d\theta}\right)_v$$

and hence prove

$$L = \theta\frac{dp}{d\theta}\left(v_2 - v_1\right)$$

(B. H. U., B.Sc., 1931.)

14. Deduce the latent heat equation

$$d\theta = \frac{\theta(v_2 - v_1)}{L}\,dp.$$

Calculate the depression of the melting point of ice per atmospheric increase of pressure, given latent heat of fusion = 80 cal. and

$$\frac{\text{density of ice at } 0°\text{C.}}{\text{density of water at } 0°\text{C.}} = \frac{10}{11}$$ (Nagpur, B.Sc., 1930.)

15. Prove that

$$\frac{dp}{d\theta} = \frac{L}{\theta(v_1 - v_2)}.$$

One gram of water-vapour at 100°C. and atmospheric pressure occupies a volume of 1640 c.c. and $L=536$ calaries. Prove that the vapour pressure of water at 99°C. is about 733 mm. of mercury. (A. U., M.Sc., 1926.)

16. If sulphur has a specific gravity 2·05 just before, and 1·95 just after melting, the melting point being 115°C. and the latent heat 9·3 find the alteration in melting point per atmospheric change of pressure. (Lond., B.Sc., Hons.)

17. Calculate the volume of a gramme of steam at 100°C., given that the latent heat of evaporation of water at 100°C. = 535 and the change of boiling point is 0·37°C. per cm. of mercury pressure ($J = 4{\cdot}2 \times 10^7$). (Manch., B.Sc.)

18. Show, on thermodynamic principles, that when a liquid film is suddenly expanded, it must fall in temperature, and find an expression for the heat that must be supplied to keep it constant. (A. U., B.Sc., Hons. 1927.)

19. Deduce an expression for the specific heat of saturated vapour and prove that in the case of water at 100°C., it is negative. How do you explain the paradox 'negative specific heat?' (A. U., B.Sc., Hons., 1931.)

20. Define the 'triple point'. Describe the successive changes observed in a system containing water at its various states when pressure is changed at a constant temperature (a) when the temperature is above the triple point, (b) when the temperature is below it. (Dacca, B.Sc., 1930.)

21. The latent heat of steam at 100°C. is 536, calculate what fraction of this heat is used up in performing external work during vaporisation, assuming the density of steam at 100°C to be 0·0007 and an atmosphere to be 10^6 dynes per sq. cm. (Manch., B.Sc.)

22. Define the 'triple point' and show that the steam line, hoar-frost line and the ice-line must meet in a single-point. Draw the isothermals of water for temperatures lower than that of the triple point. (A. U., B.Sc., 1934.)

23. Define Entropy. What is its physical significance? Show that the entropy remains constant in a reversible process but increases in an irreversible one. (A. U., B.Sc., 1936.)

24. Define Entropy. Prove from the principles of thermodynamics that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temperature under constant pressure.

Hence show that heat is generated when a substance, which expands on heating, is compressed. (A., U., B.Sc., 1938.)

25. What do you understand by 'entropy'? State the second law of thermodynamics in terms of entropy.

Calculate the change in entropy when m grams of a liquid of specific heat s are heated from $T_1°$ to $T_2°$, and then converted into its vapour without raising its temperature. [Latent heat at $T_2° = L$.] (A. U., B.Sc., 1941.)

26. Prove the latent equation

$$\frac{dL}{dT} - \frac{L}{T} = c_2 - c_1$$

Calculate the specific heat of saturated steam from the above equation and explain the meaning of its negative value. Given $L = 539·3$ cal, $T = 100°C$; $\frac{dL}{dT} = -0·640$, $c_1 = 1·01$. (Allahabad Univ., 1955; Baroda Univ. 1953.)

XI

1. State Newton's law of cooling. A copper calorimeter weighing 15 gms. is filled first with water and then with a liquid. The times taken in the two cases to cool from 65°C. to 60°C. are 170 sec. and 150 sec. respectively. The weight of the water is 11 gms and that of the liquid is 13 gms. Calculate the specific heat of the liquid. The specific heat of copper is 0·1 (Cal., B.Sc., 1928.)

2. State Stefan's law and discuss in the light of the same (1) Newton's law of cooling, (2) the temperature of the sun, and (3) the temperature of a tungsten arc. (A. U., B.Sc., 1932.)

3. State and deduce Kirchhoff's law on the emission and absorption of thermal radiation. (Sheff., B.Sc.)

4. Explain what is meant by a "perfectly black body". Write a short account of the distribution of energy in the spectrum of the radiation from such a body. (Leeds, B.Sc.)

5. Describe any furnace and explain how you would measure its temperature. (A. U., B.Sc., 1930.)

6. Discuss the principles underlying the measurement of temperatures by means of optical pyrometers, and show how the value of the temperature is estimated. Describe fully and clearly a practical form of apparatus of this type. (A. U., B.Sc., Hons., 1930.)

7. Define solar constant. Explain with necessary theory how the solar constant is determined. How is the temperature of the sun estimated from the data of the solar constant. (Allahabad Univ., 1953; Punjab Univ., 1952.)

8. Under what conditions may a thermodynamic investigation of the radiation within an enclosure be carried out?

Show that under these conditions the radiation varies as the fourth power of the temperature. (A. U., B.Sc., Hons., 1928.)

9. Describe the construction of Boys' radio-micrometer and explain the principles involved in its action. (London, B.Sc.)

10. Calculate the temperature of the Earth, assuming that it absorbs half the energy falling on it from the sun and that the sun radiates as a black body. (Radius of Sun$=7\times10^{10}$ cm ; radius of Earth$=6{\cdot}3\times10^{8}$ cm; mean radius of orbit of Earth$=1{\cdot}5\times10^{13}$ cm; temperature of sun's surface$=6000^\circ$K; Stefan's constant $\sigma=5{\cdot}7\times10^{-5}$ C.G.S. units.)

11. State Stefan-Boltzmann law of radiation and describe briefly experiments by which it has been confirmed. (A. U., B.Sc., 1934.)

12. What is a perfectly black body? How can such a body be realised in practice?

How will you verify experimentally that the ratio of the emissive and absorptive powers is the same for all bodies and is equal to the emissive power of a perfectly black body? (A. U., B.Sc., 1940.)

13. State Newton's law of cooling mentioning its limitations. How would you verify it experimentally?

A body initially at 80°C cools to 64°C in 5 minutes and to 52°C in 20 minutes. What will be its temperature after 15 minutes and what is the temperature of its surroundings? (Punjab Univ., 1951, 1952; Patna Univ., 1951.)

14. Explain what you understand by a black body. State Stefan's law of radiation and prove it from thermodynamical considerations. Indicate how it can be verified. (Punjab Univ., 1944, 1950.)

ANSWERS TO NUMERICAL EXAMPLES

I

2. 50°C. 3. 1·55:1. 4. $1·29 \times 10^5$ ergs.

II

2. 8·22 min. nearly.
6. $4·217 \times 10^7$ ergs/cal.
9. 3·39 cal. per gm. per °C.
10. (*a*) 0; (*b*) 412·8°C.
11. −15·9°C.
13. 51·8°C.
17. 228°C.
20. 1·60.
21. 1·402.

III

1. $4·22 \times 10^7$ ergs.
2. 29·5 cal.
3. $1·91 \times 10^6$ cals.
4. 9·35 h.p.; 13·1°C. per min.
5. $4·16 \times 10^7$ ergs.
6. $4·116 \times 10^7$ ergs.
7. 40·5 cal.
10. $4·66 \times 10^4$ cm./sec.
11. $5·67 \times 10^{10}$ ergs.

IV

3. 33·6°C. (*a* and *b* are given in atmospheres and c.c. respectively for 1 c.c. of gas at N.T.P.)

4. 100·5 cal. per gm.

VII

2. 475×10^{-7}. 3. 5·646 sec. per day gain per °C. rise.

4. 59·6 sec. 6. $0·8 \times 10^{-4}$ per °C. 7. $\frac{5}{36}$.

VIII

2. 105·4°C.
3. $11·3 \times 10^8$ cal.
4. 139·936°C; 448 gm.
5. 0·39 cm. per hour; 19 hours
11. $1·31 \times 10^{-3}$.
12. $1·26 \times 10^{-5}$ C.G.S. units.
14. $3·54 \times 10^{-4}$.
16. $1·13 \times 10^{-4}$ C.G.S. units.

X

1. $\frac{1}{6·6 \times 10^5}$ 2. $6·28 \times 10^8$ ergs. 8. 0·36 units

14. 0·0081°C. 16. 0·0252°C. 17. 1674 c.c. 21. $\frac{1}{15·8}$

26. −1·07.

XI

1. 0·733. 10. 290°K. 13. 43°C; 16°C

PHYSICAL CONSTANTS*

The Gas Constant	$R = (8{\cdot}31436 \pm 0{\cdot}00038) \times 10^{7}$ ergs. deg.$^{-1}$ mole^{-1}.
	$= 1{\cdot}98646 \pm 0{\cdot}00021$ cal. deg.$^{-1}$ mole^{-1}.
Coefficient of expansion for perfect gas at 0°C.	$= 0{\cdot}0036608$ per °C.
Ice point	$= 273{\cdot}16 \pm 0{\cdot}01$°K.
Volume of one gram-molecule at N. T. P.	$= 22{\cdot}414$ litres
Avogadro number	$N = (6{\cdot}0228 \pm 0{\cdot}0011) \times 10^{23}$ mole^{-1}
Loschmidt number	$n = (2{\cdot}6870 \pm 0{\cdot}0005) \times 10^{19}$ cm.$^{-3}$
Mass of H^1 atom	$M = (1{\cdot}67339 \pm 0{\cdot}00031) \times 10^{-24}$ gm.
Standard gravity	$g = 980{\cdot}665$ cm. sec.$^{-2}$
Density of mercury at N.T.P.	$= 13{\cdot}59504 \pm 0{\cdot}00005$ gm. cm^{-3}
Standard atmosphere	$= 1{\cdot}013246 \times 10^{6}$ dynes cm^{-2}
Mechanical equivalent of heat	$J = (4{\cdot}1855 \pm 0{\cdot}0004) \times 10^{7}$ ergs cal.$^{-1}$
Boltzmann's constant	$k = (1{\cdot}38047 \pm 0{\cdot}00026) \times 10^{-16}$ ergs. °C^{-1}
Stefan-Boltzmann constant	$\sigma = (5{\cdot}672 \pm 0{\cdot}003) \times 10^{-5}$ erg. cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$
Wien's constant	$b = 0{\cdot}28971 \pm 0{\cdot}00007$ cm. degree
Planck's constant	$h = (6{\cdot}624 \pm 0{\cdot}002) \times 10^{-27}$ erg. sec.
Velocity of light in vacuum	$c = (2{\cdot}99776 \pm 0{\cdot}00004) \times 10^{10}$ cm. sec.$^{-1}$
Electronic charge	$e = (2{\cdot}99776 \pm 0{\cdot}0010) \times 10^{-10}$ e.s.u.
	$= (1{\cdot}60203 \pm 0{\cdot}00034) \times 10^{-20}$ e.m.u.
Faraday number	$F = 96501 \pm 10$ int. coul. per gm. equiv.
Mass of the electron	$m = (9{\cdot}1066 \pm 0{\cdot}0032 \times 10^{-28}$ gm.
Specific electronic charge	$e/m = (1{\cdot}7592 \pm 0{\cdot}0005) \times 10^{7}$ e. m. u. per gm.
Gravitation constant	$G = (6{\cdot}670 \pm 0{\cdot}005) \times 10^{-8}$ dyne cm.^{2} gm.$^{-2}$

*The values given here are taken from Birge, *Reviews of Modern Physics*, Vol. 13, p. 233 (1941); *Amer. Jour. Phys.*, Vol. 13, p. 63 (1945). All quantities in this table involving the mole or the gram equivalent are on the chemical scale of atomic weight (O = 16·0000).

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